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(71) Applicant: **THE C.P. HALL COMPANY** [US/US]; 311
South Wacker Drive, Suite 4700, Chicago, IL 60606-6622
(US).

(72) Inventors: **WENTWORTH, Gary**; 5540 North Wayne
Avenue, Chicago, IL 60640 (US). **O'ROURKE, Stephen**;
1847 Marne Road, Bolingbrook, IL 60490 (US). **STE-
FANISIN, Kimberly**; 4867 Wick Drive, Oak Lawn, IL
60453 (US). **ENGLISH, John**; 11000 S. Keeler, Oak
Lawn, IL 60453 (US).

(74) Agent: **ANDERSON, Richard, H.**; Marshall, Gerstein
& Borun, 6300 Sears Tower, 233 South Wacker Drive,
Chicago, IL 60606 (US).

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(54) Title: ADHESION PROMOTER FOR CORD-REINFORCED RUBBER AND METAL OR POLYMER SUBSTRATE/RUB-
BER COMPOSITES

(57) Abstract: A rubber composition including a natural or synthetic rubber, and an adhesive resin capable of unexpected adhesion
to metal, polymer and glass substrates, particularly cords in radical tires, hoses, conveyor belts, transmission belts, and the like by
the addition of long chain esters, including mono, di- and tri-esters.

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ADHESION PROMOTER FOR CORD-REINFORCED RUBBER AND METAL OR POLYMER SUBSTRATE/RUBBER COMPOSITES

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial No. 10/301,770, filed November 21, 2002, which is a continuation-in-part of U.S. Patent Application Serial No. 10/144,229, filed May 10, 2002, the entire respective disclosures of which are hereby incorporated by reference.

FIELD OF THE INVENTION

The present invention is directed to adhesion promoters for adhering elastomers, including natural and/or synthetic rubbers, to natural or synthetic polymeric cord or fabric substrates, and/or metal cord or metal substrates, particularly cords in the manufacture of cord-reinforced rubber articles, such as tires, hoses, conveyor belts, transmission belts, and the like.

BACKGROUND OF THE INVENTION

Many rubber articles, principally automobile tires, but also including hoses, conveyor belts, power train belts, *e.g.*, transmission belts, and the like, are usually reinforced with fibrous or metal cords. In all such instances, the fiber must be firmly bonded to the rubber. This is so whether the fiber is a natural or synthetic polymer, or metallic, and whether the rubbers are natural or synthetic.

The conventional practice has been to prepare the fiber by pretreatment with a combination of hexamethoxymelamine or hexamethylene-tetramine and phenol-formaldehyde condensation product, wherein the phenol is almost always resorcinol. By a mechanism not completely understood, the resin reacts with the fiber and the rubber, effecting a firm reinforcing bond.

One method for preparing rubber compositions reinforced with cords entails compounding a vulcanizing rubber stock composition with the components of an adhesive resin condensation product. The components of the condensation product include a methylene acceptor and a methylene donor. The most commonly employed methylene acceptor is a phenol, such as resorcinol, while the most commonly employed methylene donor is a melamine, such as N-(substituted oxymethyl)melamine. The effect achieved is resin formation *in-situ* during vulcanization of the rubber, creating a bond between the metal or polymeric cords and the rubber, irrespective of whether the cords have been pretreated

with an additional adhesive, such as a styrene-butadiene latex, polyepoxides with a blocked isocyanate, and the like.

Resorcinol-free vulcanizable rubber compositions are known. For example, U.S. Patent No. 5,298,539 discloses vulcanizable rubber compositions containing uncured rubber, a vulcanizing agent and at least one additive selected from the group consisting of derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril monomer and oligomers of these monomers. These derivatives are substituted on average at two or more positions on the monomer or each unit of the oligomer with vinyl terminated radicals and the composition is free of resorcinol.

Another manner of eliminating resorcinol from vulcanizable rubber compositions has relied on the use of alternative coreactants. U.S. Patent No. 4,038,220 describes a vulcanizable rubber composition which comprises a rubber, a filler material, N-(substituted oxymethyl)melamine and at least one of α - or β -naphthol. This reference employs the monohydric phenols, α - or β -naphthol, as methylene acceptors in the resin forming reaction during vulcanization in the absence of resorcinol. The use of resorcinol-formaldehyde resin to replace resorcinol in vulcanizable rubber compositions is also known. For example, *see* A. Peterson, et al., "Resorcinol Bonding Systems for Steel Cord Adhesion", Rubber World (August 1984).

An increased need in the industry for fiber reinforcing of rubber to survive high dynamic stress, such as flexing, to avoid tire belt separation has brought about a continuing search for other and better methods for achieving high adhesive strength.

Tires typically have a construction such that a carcass, edge portions of a belt, an under-belt pad and the like are intricately combined with each other in its shoulder portion. The under-belt pad provided continuously along the circumferential shoulder portion of the tire between a tread rubber portion and the carcass and extending outwardly of the belt edge portions along the width of the tire is a thick rubber layer, which is a structural characteristic for alleviating a shear stress possibly generated between the belt edge portions and the carcass. Further, since the under-belt pad is repeatedly subjected to loads during running, heat is liable to build-up in the under-belt pad, thereby causing internal rubber destruction in the under-belt pad and adhesion failures between the rubber components and between a rubber portion and cords (steel cords) in the carcass. This causes separation of the belt edge portions and ply separation in the carcass resulting in breakdown of the tire. One conventional approach to this problem is that the under-belt pad is formed of a rubber compound which contains a reduced amount of carbon black for suppression of heat build-up.

However, the rubber compound for the under-belt pad is softened by the reduction of the carbon black content therein. This also results in the adhesion failure and the internal rubber destruction in the under-belt pad due to the heat build-up, thereby causing the ply separation and the belt separation in the tire during running. Therefore, this approach is not satisfactory in terms of the durability of the tire. The deterioration of the durability of the tire which results from the heat build-up attributable to the structural characteristic of the under-belt pad is a more critical problem, since the recent performance improvement of automobiles requires that tires have a higher durability under higher speed running and heavy loads.

Despite their good abrasion resistance, radial tires become unusable sooner than bias tires because of the belt separation which takes place while the tread still remains. One way that this problem has been addressed is by improving the tread or steel cord-embedding rubber. For example, an improved tread is of dual layer structure, with the inner layer (base tread adjacent to the belt) being made of a rubber composition which is saved from heat generation at the sacrifice of abrasion resistance, and the outer layer (cap tread) being made of a rubber composition of high abrasion resistance. Also, an improved steel cord-embedding rubber is made of a rubber composition containing an adhesive such as a cobalt salt of an organic acid, hydroxybenzoic acid, and resorcinol, which increases adhesion between rubber and steel cord. These improvements, however, are not completely successful.

Other adhesion promoters have been used in an attempt to avoid belt separation, for example, special latices such as, for example, a vinyl-pyridine latex (VP latex) which is a copolymer of about 70% butadiene, about 15% styrene and about 15% 2-vinylpyridine. Examples of other latices which are present in adhesion promoters are acrylonitrile rubber latices or styrene-butadiene rubber latices. These can be used as such or in combination with one another. Especially suitable adhesion promoters for polyesters are also those which are applied in multi-stage processes, for instance a blocked isocyanate being applied in combination with polyepoxide and the material then being treated using customary resorcinol-formaldehyde resins (RFL dip). It is also known to use combinations of RFL dips with other adhesion-promoting substances such as, for example, a reaction product of triallyl cyanurate, resorcinol and formaldehyde or p-chlorophenol, resorcinol and formaldehyde.

Not only is it necessary that adhesion between rubber and metal, *e.g.*, steel or polymeric cord be high, but it is also necessary that a decrease in adhesion be as small as possible while tires are in use. In actuality, tires containing a steel cord-embedding rubber with good adhesion occasionally lose the initial adhesion to a great extent after use. The

following are the possible reasons why adhesion between steel cord and rubber decreases while tires are in use:

(1) Tires are subject to many minute cuts when they run over gravel or sharp objects. The cuts reaching the inside of the tread permit air and moisture to infiltrate into the tire, promoting the aging and fatigue of the embedding rubber and also rusting the steel cord. All this leads to a decrease in adhesion.

(2) The adhesion improver incorporated into the steel cord-embedding rubber diffuses and migrates into the tread rubber during vulcanization or tire use. This leads to a decrease in adhesion.

(3) The softener and other additives incorporated into the tread migrate into the steel cord-embedding rubber. This also leads to a decrease in adhesion.

Despite the various proposals made to improve the adherence of cord to rubber in vulcanizable rubber compositions, there is a continuing need for commercially available cost effective additives that improve the adhesion of rubber to fibrous or metal cords in vulcanizable rubber compositions.

The adhesion promoter systems of the present invention far surpass any extant adhesion promoters known in the art for adhesion of metal and/or polymeric cord to vulcanizable rubber.

SUMMARY OF THE INVENTION

In brief, it has been found that the use of long chain esters formed by reacting mono-, di-, and/or tri-carboxylic acids containing one, two, or three C_6-C_{24} long chain radicals or fatty acid residues, and alcohols containing a C_3-C_{24} alkyl group, in a natural or synthetic vulcanizable rubber, unexpectedly increases the adhesion between the rubber and a metal or polymeric substrate, such as metal or polymeric surfaces, particularly cords used in reinforcing rubber in tires, hoses, conveyor belts, motor mounts, automotive drive train belts, including transmission belts, and the like, when added with an adhesive resin, such as a melamine-containing resin or a phenol-, *e.g.*, resorcinol-containing resin, *e.g.*, a Novolak resin. Examples of suitable substrates include steel, brass-coated steel, brass, polyester, Aramid, textiles, copper, glass, and the like. Application of the adhesive promoters of the invention is particularly contemplated with steel cord, brass-coated steel cord, brass cord, polyester fiber cord, Aramid fiber cord, glass cord, fabric and flat metal surfaces, and the like. While these resins have been used before to adhere metal tire cord to a vulcanizable rubber, and theoretically bond the rubber to the resin, surprisingly good adhesion has been found by

additionally adding one or more long chain mono-, di-, and/or tri-esters, particularly dimerate esters reacted from C₁₈ fatty acids, and C₃-C₂₄ alcohols, preferably, C₃-C₁₈ alcohols, more preferably C₆-C₁₈ alcohols. Preferably, the esters provide unexpected, tenacious bonding between polymeric or metal cord and rubber, when combined with an adhesive resin. It is theorized that the long chain esters of the invention strongly adhere both to the rubber and to the resin, with the resin providing sufficient ionic bonding to the reinforcing cords.

One aspect of the composition and articles described herein is to provide a radial tire for heavy load vehicles characterized by good adhesion between steel or polymeric cord and steel cord-embedding rubber, said adhesions lasting for a long time with only a small loss of adhesion while tires are in use. Another aspect of the compositions and articles described herein is to provide a radial tire for vehicles and other cord-embedded rubber articles which are superior in cord adhesion to rubber.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The adhesion promoter systems of the invention include at least one long chain ester compound and at least one adhesive resin. The adhesion promoter systems are useful for improving the adhesion of rubber to metal and polymeric substrates, particularly metal and polymeric cord. Surprisingly, the adhesion promoter systems disclosed herein significantly increase the adhesion of rubber compositions to such metal and polymeric substrates. In the description, the terms "adhesion promoter system" and "adhesion promoter" may be used interchangeably.

In the adhesion promoter systems of the invention, long chain esters are typically added to natural or synthetic rubber with a vulcanizing agent and an adhesive resin. The adhesion promoter systems may be added to a natural and/or synthetic rubber(s), as a neat liquid, in order to promote adhesion. Typically, however, the adhesion promoters are mixed with a dry carrier, such as calcium silicate, to form an alternative delivery system, which can be incorporated into natural and/or synthetic rubber(s). In such a method, the carrier facilitates delivery of the active adhesion promoting agents to the rubber(s). In yet another refinement of the invention, the adhesion promoter may be formulated as a "polymer masterbatch." According to this aspect of the invention, a pellet comprising polymer (about 6 wt.% to about 20 wt.%), filler or inert ingredients (about 0 wt. % to about 14 wt.%), with the balance being an adhesion promoter system (*i.e.*, at least one ester compound in accordance with formulas I-IV and at least one adhesive resin such as melamine) is added to a natural or synthetic rubber. Typically, the masterbatch polymer and the rubber to which the

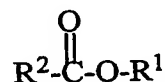
masterbatch polymer is added are miscible. Preferably, the masterbatch polymer and the rubber are the same.

Throughout the specification, the adhesion promoter systems are generally used in an amount between about 0.2% by weight and about 30% by weight. Typically, each component of an adhesion promoter system of the invention (*i.e.*, an ester in accordance with formulas I-IV and an adhesive resin) is present in an amount between about 0.1% and about 15% by weight, usually between about 1 wt.% and about 10 wt.%, and most preferably between about 2 wt.% and about 8 wt.%, based on the weight of natural and synthetic rubber in the composition.

Ranges may be expressed herein as from "about" or "approximately" one particular value and/or to "about" or "approximately" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment.

The long chain esters may be monoesters, diesters, triesters, or mixtures thereof, that may include saturated or unsaturated hydrocarbon chains, straight chain or branched having none, one, two or three double bonds in the hydrocarbon chains.

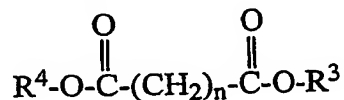
The monoesters have a formula I, as follows:



(I)

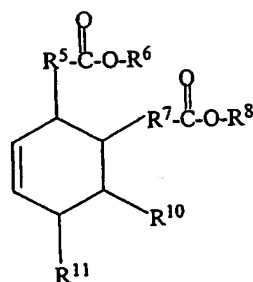
wherein R^1 is a C_3 - C_{24} alkyl, preferably C_3 - C_{18} alkyl, more preferably C_6 - C_{18} alkyl, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds. R^2 is a C_3 - C_{24} , preferably C_6 - C_{24} , more preferably C_8 - C_{18} saturated hydrocarbon, or an unsaturated hydrocarbon having 1 to 6, preferably 1 to 3 carbon-to-carbon double bonds.

The diesters have a formula II or III, as follows:



(II)

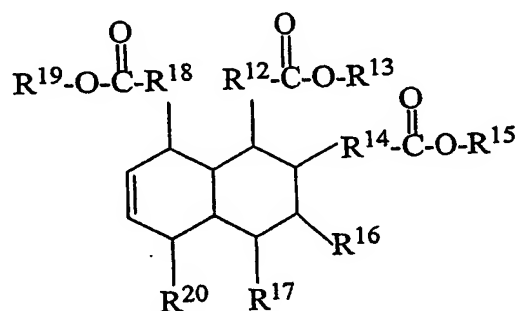
wherein $n=3-24$, preferably 6-18, and more preferably 3-10, and R^3 and R^4 , same or different, are C_3 - C_{24} alkyl, preferably C_3 - C_{18} alkyl, more preferably C_6 - C_{18} alkyl radicals, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.



(III)

wherein R^5 and R^7 , same or different, are C_3 - C_{24} alkyl, preferably C_6 - C_{24} alkyl, more preferably C_8 - C_{18} alkyl, straight chain or branched, either saturated or containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds;
 R^6 and R^8 , same or different, are C_3 - C_{24} alkyl, preferably C_3 - C_{18} alkyl, more preferably C_6 - C_{18} alkyl, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and
 R^{10} and R^{11} , same or different, are C_3 - C_{24} saturated hydrocarbon chains, preferably C_3 - C_{18} , more preferably C_6 - C_{18} , straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon chains, preferably C_3 - C_{18} , more preferably C_6 - C_{18} , straight chain or branched, containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds.

The triesters have a formula IV, as follows:



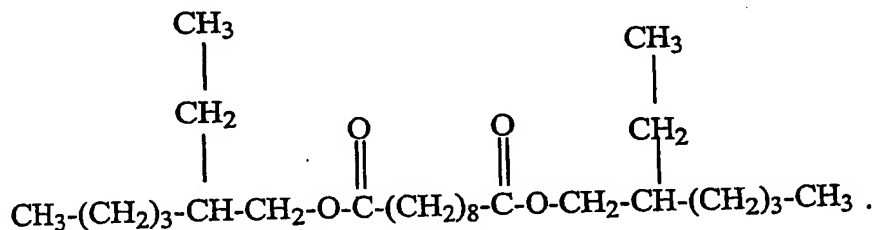
(IV)

wherein R^{12} , R^{14} and R^{18} , same or different, are C_3 - C_{24} alkyl, preferably C_6 - C_{24} alkyl, more preferably C_8 - C_{18} alkyl, straight chain or branched, either saturated or containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds;
 R^{13} , R^{15} and R^{19} , same or different, are C_3 - C_{24} alkyl, preferably C_3 - C_{18} alkyl, more preferably C_6 - C_{18} alkyl, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and
 R^{16} , R^{17} and R^{20} , same or different, are C_3 - C_{24} saturated hydrocarbon chains, preferably C_3 - C_{18} , more preferably C_6 - C_{18} , straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon

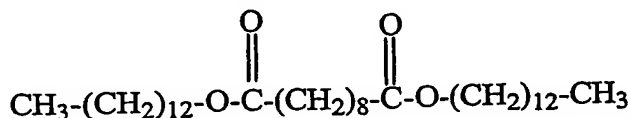
chains, preferably C_3 - C_{18} , more preferably C_6 - C_{18} , straight chain or branched, containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds.

The fatty acid residues or hydrocarbon chains R^2 , R^5 , R^7 , R^{12} , R^{14} and R^{18} of the esters of formulas I, II, III, and IV can be any C_3 - C_{24} , preferably C_6 - C_{24} , more preferably C_8 - C_{18} , hydrocarbon chain, either saturated or containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds, derived from animal or vegetable fatty acids such as butter; lard; tallow; grease; herring; menhaden; pilchard; sardine; babassu; castor; coconut; corn; cottonseed; jojoba; linseed; oiticica; olive; palm; palm kernel; peanut; rapeseed; safflower; soya; sunflower; tall; and/or tung. Examples are the hydrocarbon chain residues from the following fatty acids, where the number in parentheses indicates the number of carbon atoms, and the number of double bonds, *e.g.*, (C_{24-6}) indicates a hydrocarbon chain having 24 carbon atoms and 6 double bonds: Hexanoic (C_{6-0}); Octanoic (C_{8-0}); Decanoic (C_{10-0}); Dodecanoic (C_{12-0}); 9-Dodecenoic (CIS) (C_{12-1}); Tetradecanoic (C_{14-0}); 9-Tetradecenoic (CIS) (C_{14-1}); Hexadecanoic (CIS) (C_{16-0}); 9-Hexadecenoic (CIS) (C_{16-1}); Octadecanoic (C_{18-0}); 9-Octadecenoic (CIS) (C_{18-1}); 9-Octadecenoic, 12-Hydroxy-(CIS) (C_{18-2}); 9, 12-Octadecadienoic (CIS, CIS) (C_{18-2}); 9, 12, 15 Octadecatrienoic (CIS, CIS, CIS) (C_{18-3}); 9, 11, 13 Octadecatrienoic (CIS, TRANS, TRANS) (C_{18-3}); 9, 11, 13 Octadecatrienoic, 4-Oxo (CIS, TRANS, TRANS) (C_{18-3}); Octadecatetrenoic (C_{18-4}); Eicosanoic (C_{20}); 11-Eicosenoic (CIS) (C_{20-1}); Eicosadienoic (C_{20-2}); Eicosatrienoic (C_{20-3}); 5, 8, 11, 14 Eicosatetraenoic (C_{20-4}); Eicosapentaenoic (C_{20-5}); Docosanoic (C_{22}); 13 Docosenoic (CIS) (C_{22-1}); Docosatetraenoic (C_{22-4}); 4, 8, 12, 15, 19 Docosapentaenoic (C_{22-5}); Docosahexaenoic (C_{22-6}); Tetracosenoic (C_{24-1}); and 4, 8, 12, 15, 18, 21 Tetracosahexaenoic (C_{24-6}).

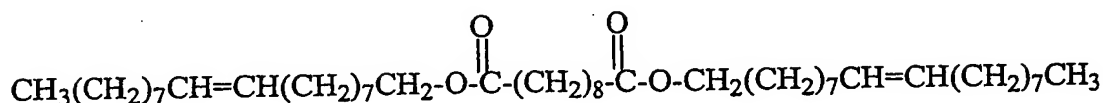
Examples of particularly useful diesters of formula II include a saturated diester formed by the reaction of sebacic acid and 2-ethylhexyl alcohol:



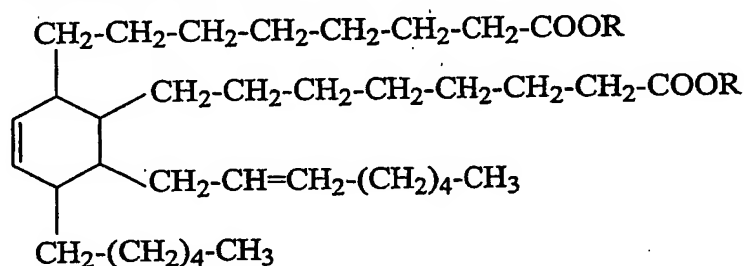
Other useful diesters falling within formula II include the saturated diester formed by the reaction of sebacic acid with tridecyl alcohol,



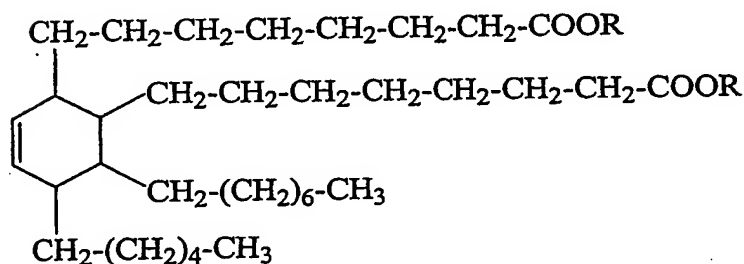
and the unsaturated diester formed by reaction of sebacic alcohol with oleyl alcohol:



Useful cyclic diesters falling within formula III include dimerate ester structures formed by the reaction of a C₃₆ dimer acid derived from tall oil fatty acids and C₃-C₂₄, preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohol, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds. Examples of such cyclic esters include the following structures, wherein the dimer acid corresponding to structure A is formed by self reaction of linoleic acid, the dimer acid corresponding to structure B is formed by reacting linoleic acid with oleic acid, and the dimer acid corresponding to structure C is formed by reacting linoleic acid with linolenic acid:

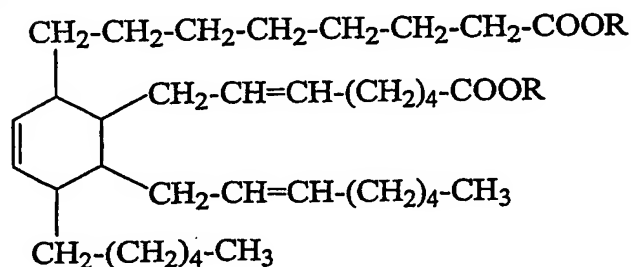


(A);



(B);

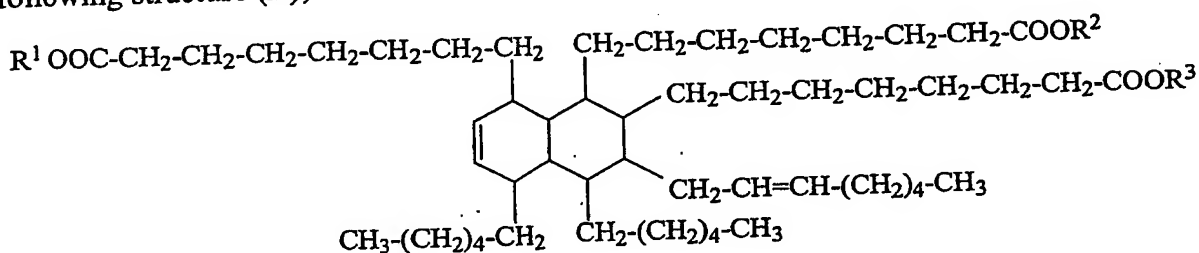
and



(C);

wherein each R, same or different, in formulas (A), (B), and (C) is a C₃-C₂₄ radical, preferably C₃-C₁₈, more preferably C₆-C₁₈, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds. RX-13804 is another example of an unsaturated diester (dimerate ester) formed by the reaction of a predominantly C₃₆ dimer acid reacted with 2-ethylhexyl alcohol. RX-13824 is an additional unsaturated diester (dimerate ester) formed by the reaction of a predominantly C₃₆ dimer acid with tridecyl alcohol.

A representative example of the triester (trimerate ester) of formula IV is the following structure (D);



(D);

wherein each R¹, R², and R³, same or different, is a C₃-C₂₄ radical, preferably C₃-C₁₈, more preferably C₆-C₁₈, straight chain, or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

A particularly useful blend of long chain esters is formed from blends of mono, dimer, and trimer acids, for example, products having CAS#: 61788-89-4. Esters prepared from such products are blends including, primarily, the above C₃₆ and C₅₄ dimerate and trimerate esters (A), (B), (C) and (D), shown in the above structures, that is predominantly (more than 50% by weight) the C₃₆ dimerate esters (A), (B) and (C).

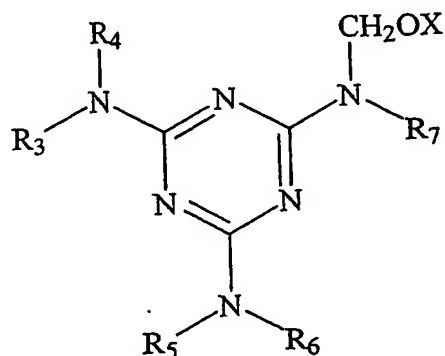
Commercially available blends of useful polybasic acids that can be reacted with C₃-C₂₄, preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohols, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds to produce the dimerate and trimerate esters, as blends, include the following: EMPOL[®] 1010 Dimer Acid; EMPOL[®] 1014 Dimer Acid; EMPOL[®] 1016 Dimer Acid; EMPOL[®] 1018 Dimer Acid; EMPOL[®] 1022 Dimer Acid; EMPOL[®] 1024 Dimer Acid; EMPOL[®] 1040 Trimer Acid; EMPOL[®] 1041 Trimer Acid; EMPOL[®] 1052 Polybasic Acid; and similar PRIPOL[™] products from Uniqema as well as UNIDYME[®] products from Arizona Chemical.

Particularly useful long chain ester additives are made by reacting any of the long chain mono, dimer and/or trimer acids with one or more straight chain or branched C₃-C₂₄,

preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohols to produce the esters of formulas I, II, III and IV. The above dimer, trimer, and polybasic acids are produced by dimerizing, trimerizing, and polymerizing (oligomerizing) long chain carboxylic acids from the above-mentioned fatty acids. The fatty acids may be mixtures. Accordingly, the dimer acid produced by dimerizing a C₁₈ carboxylic acid (typically, a mixture of stearic, oleic, linoleic, and linolenic), after esterification, will result in a blend of numerous dimerate and trimerate esters in accordance with formulas III and IV, including saturated and unsaturated esters (*i.e.*, some long chain esters may contain hydrocarbon chains having 1 to 6, generally 1 to 3, carbon-to-carbon double bonds). Any one, or any blend, of the esters of formulas I, II, III and/or IV, when combined with an adhesive resin, will function to increase the adhesion of natural or synthetic rubber to metal or polymeric cord, metal or polymeric substrates, such as polymeric woven or non-woven fabrics, and metal flat stock materials.

The adhesion promoters include an adhesive resin, which preferably is a condensation product of a formaldehyde or methylene donor and a formaldehyde or methylene acceptor, either pre-condensed, or condensed *in-situ* while in contact with the rubber. The term "methylene donor" is intended to mean a compound capable of reacting with a methylene acceptor (such as resorcinol or its equivalent containing a reactive hydroxyl group) and generate the resin outside of the rubber composition, or *in-situ*. Preferably, the components of the condensation product include a methylene acceptor and a methylene donor. The most commonly employed methylene acceptor is a phenol, such as resorcinol, while the most commonly employed methylene donor is a melamine, such as N-(substituted oxymethyl)melamine. The effect achieved is resin formation *in-situ* during vulcanization of the rubber, creating a bond between the metal or polymeric cords and the rubber, irrespective of whether the cords have been pretreated with an additional adhesive, such as a styrene-butadiene latex, polyepoxides with a blocked isocyanate, and the like. The long chain ester additive/resin combinations described herein are particularly useful with steel cord, where adhesive pretreatment has been largely ineffective.

Examples of methylene donors which are suitable for use in the rubber compositions disclosed herein include melamine, hexamethylenetetramine, hexaethoxymethylmelamine, hexamethoxymethylmelamine, lauryloxymethyl-pyridinium chloride, ethoxymethylpyridinium chloride, trioxan hexamethoxy-methylmelamine, the hydroxy groups of which may be esterified or partly esterified, and polymers of formaldehyde, such as paraformaldehyde. In addition, the methylene donors may be N-substituted oxymethylmelamines, of the general formula:



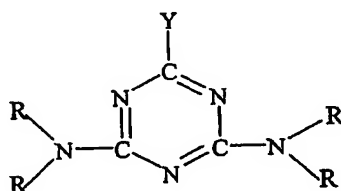
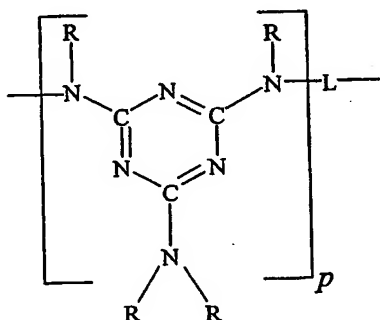
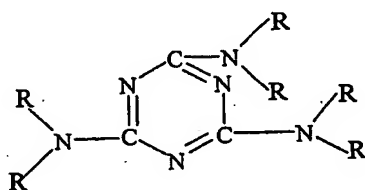
wherein X is an alkyl having from 1 to 8 carbon atoms R^3 , R^4 , R^5 , R^6 and R^7 are individually selected from the group consisting of hydrogen, an alkyl having from 1 to 8 carbon atoms and the group $-CH_2OX$. Specific methylene donors include hexakis(methoxymethyl)melamine; N,N',N'' -trimethyl/ N,N',N'' -trimethylol-melamine; hexamethylolmelamine; N,N',N'' -dimethylolmelamine; N -methylol-melamine; NN' -dimethylolmelamine; N,N',N'' -tris(methoxymethyl)melamine; and N,N',N'' -tributyl- N,N',N'' -trimethylol-melamine. The N -methylol derivatives of melamine are prepared by known methods.

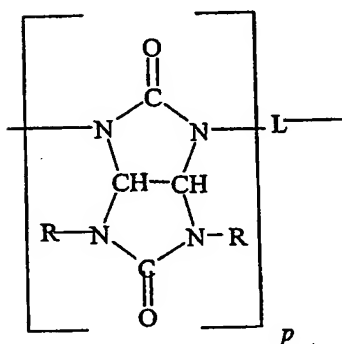
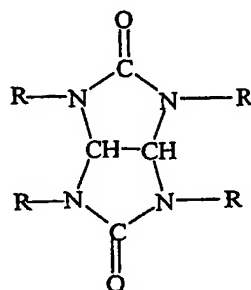
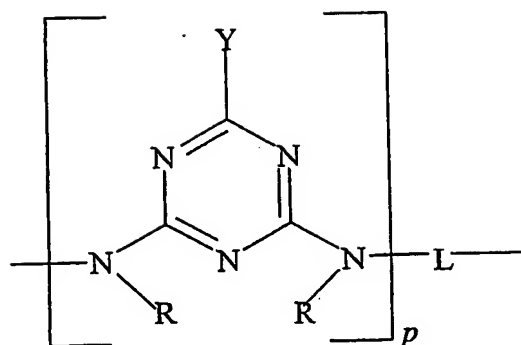
The amount of methylene donor and methylene acceptor, pre-condensed or condensed *in-situ*, that are present in the rubber composition may vary. Typically, the amount of pre-condensed methylene donor and methylene acceptor is present will range from about 0.1% to about 15.0%; or each can be added separately in an amount of about 0.1% to about 10.0%, based on the weight of natural and/or synthetic rubber in the composition. Preferably, the amount of each of a methylene donor and methylene acceptor added for *in-situ* condensation ranges from about 2.0% to about 5.0%, based on the weight of natural and/or synthetic rubber in the composition. The weight ratio of methylene donor to the methylene acceptor may vary. Generally speaking, the weight ratio will range from about 1:10 to about 10:1. Preferably, the weight ratio ranges from about 1:3 to 3:1.

Resorcinol-free vulcanizable rubber compositions also are useful in the rubber compositions described herein. For example, resorcinol-free adhesive resins and adhesive compounds useful in the adhesion promoter systems (*i.e.*, when combined with the long chain esters described herein) include those described in U.S. Patent Nos. 5,891,938 and 5,298,539, both hereby incorporated by reference. The '938 patent discloses vulcanizable rubber compositions containing an uncured rubber and a self-condensing alkylated triazine resin having high imino and/or methylol functionality. U.S. Patent No. 5,298,539 discloses rubber additives which are substituted derivatives based on cyclic nitrogen compounds such as melamine, acetoguanamine, cyclohexylguanamine, benzoguanamine, and similar alkyl, aryl

or aralkyl substituted melamines, glycoluril and oligomers of these compounds. In particular, the adhesive resins and adhesive compounds which are useful as the adhesive resins in the rubber compositions described herein include the following: adhesive resins selected from the group consisting of derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril monomers and oligomers of these monomers, which have been substituted on average at two or more positions on the monomer or on each unit of the oligomer with vinyl terminated radicals, the vulcanizable rubber composition being free of resorcinol; and, these derivatives which have been further substituted on average at one or more positions with a radical which comprises carbamylmethyl or amidomethyl.

Further, the adhesive resin can be any of the compounds of the following formulas:





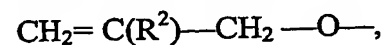
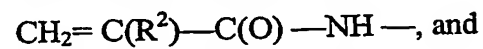
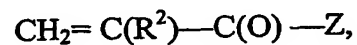
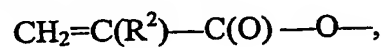
and positional isomers thereof,

wherein, in each monomer and in each polymerized unit of the oligomers, Y is selected from methyl, phenyl and cyclohexyl, and, on average,

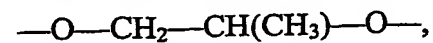
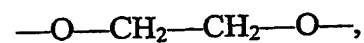
at least two R are $-\text{CH}_2-\text{R}^1$,

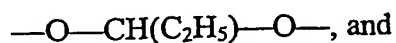
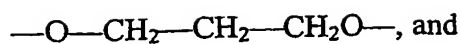
and any remaining R are H, and

at least 2 R^1 are radicals selected from:

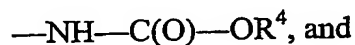
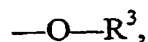


wherein R^2 is hydrogen or C_1 - C_{18} alkyl, and Z is a radical selected from:





any remaining R^1 radicals are selected from



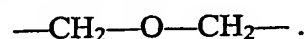
wherein R_3 is hydrogen or R_4 , and

R_4 is a C_1 - C_{18} alkyl, alicyclic, hydroxyalkyl, alkoxyalkyl or aromatic radical, and

in the oligomers,

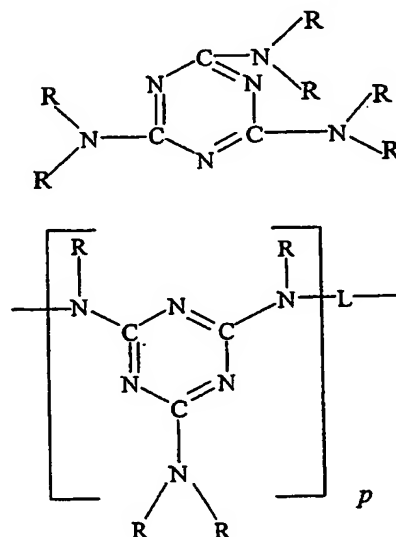
P is 2 to about 10, and

L is methylene or the radical

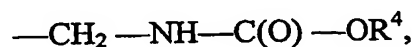


These adhesive compounds are particularly useful, wherein on average at least one R^1 in each monomer or in each oligomerized unit is —NH—C(O)—OR^4 ,

particularly the compounds of the following formulas:

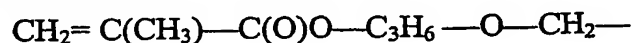


Particularly useful adhesive resins include the above formulas wherein on average, at least one R radical in each monomer or in each oligomerized unit is

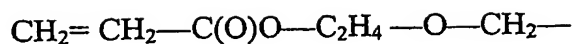


wherein R^4 is a C_1 - C_{18} alkyl, alicyclic, hydroxyalkyl, alkoxyalkyl or aromatic radical, and

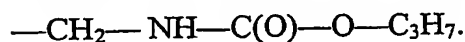
wherein, on average, at least two R radicals are selected from



and



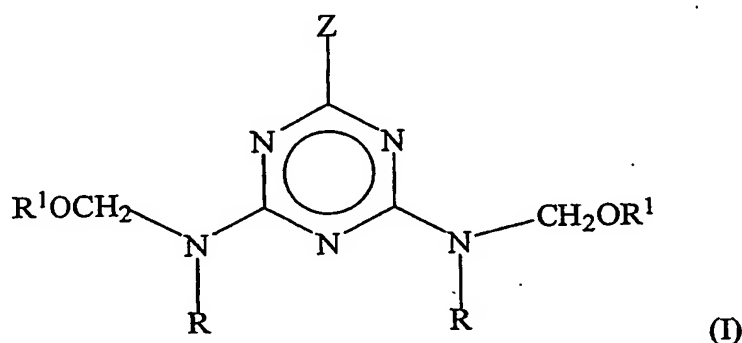
and at least one R radical is selected from



These adhesive resins and compounds can include additional additives, particularly those selected from hydroxymethylated and alkoxymethylated (alkoxy having 1-5 carbon atoms) derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril and their oligomers.

Additional adhesive resins useful in the rubber compositions described herein include self-condensing alkylated triazine resins selected from the group consisting of (i), (ii), and (iii):

(i) a self-condensing alkylated triazine resin having at least one of imino or methylol functionality and represented by the formula (I)



(ii) an oligomer of (i), or

(iii) a mixture of (i) and (ii), wherein

Z is $-\text{N}(\text{R})(\text{CH}_2\text{OR}^1)$, aryl having 6 to 10 carbon atoms, alkyl having 1 to 20 carbon atoms or an acetyl group,

each R is independently hydrogen or $-\text{CH}_2\text{OR}^1$, and

each R^1 is independently hydrogen or an alkyl group having 1 to 12 carbon atoms, provided that at least one R is hydrogen or $-\text{CH}_2\text{OH}$ and at least one R^1 is selected from the alkyl group; and

wherein the vulcanizable rubber composition is substantially free of methylene acceptor coreactants.

These adhesive resins are particularly useful wherein at least one R group is hydrogen and/or wherein at least one R^1 group is a lower alkyl group having 1 to 6 carbon atoms, particularly where the adhesive resin is a derivative of melamine, benzoguanamine, cyclohexylguanamine, or acetoguanamine, or an oligomer thereof.

One particularly useful alkylated triazine adhesive resin of the above formula is wherein Z is $-N(R)(CH_2OR^1)$.

Another manner of eliminating resorcinol in an adhesive resin for rubber compositions, also useful herein, is N-(substituted oxymethyl)melamine and at least one of α - or β -naphthol. This adhesive resin employs the monohydric phenols, α - or β -naphthol, as methylene acceptors in the resin forming reaction during vulcanization in the absence of resorcinol.

Other adhesive resins useful in the rubber compositions described herein include special latices such as, for example, a vinyl-pyridine latex (VP latex) which is a copolymer of about 70% butadiene, about 15% styrene and about 15% 2-vinylpyridine; acrylonitrile rubber latices; and styrene-butadiene rubber latices. These can be used as such or in combination with one another. Another suitable adhesive resin useful herein, particularly for polyesters, are those which are applied in multi-stage processes, for instance a blocked isocyanate being applied in combination with polyepoxide and the material then being treated using customary resorcinol-formaldehyde resins (RFL dip). Additional useful adhesive resins include combinations of RFL dips with other adhesion-promoting substances such as, for example, a reaction product of triallyl cyanurate, resorcinol and formaldehyde or p-chlorophenol, resorcinol and formaldehyde.

Other suitable adhesive resins for use in the rubber and adhesion promoters described herein include polyurethane resins, epoxy resins, phenol aldehyde resins, polyhydric phenol aldehyde resins, phenol furfural resins, xylene aldehyde resins, urea formaldehyde resins, melamine formaldehyde resins, alkyd resins, polyester resins, and the like.

Typically, in the adhesion promoter systems, at least one ester compound in accordance with formulas I-IV is combined with an adhesive resin in a weight ratio between about 10 parts ester to about 1 part adhesive resin (*i.e.*, a ratio of about 10:1, ester to resin, respectively) and about 1 part ester to about 10 parts resin (*i.e.*, a ratio of about 1:10, ester to resin, respectively). More preferably, the esters are combined with an adhesive resin in a weight ratio between about 4 parts ester to about 1 part adhesive resin and about 1 part ester to about 4 parts resin. Most preferably, the ratio of ester to adhesive resin is approximately one to one in the adhesion promoter systems of the invention.

The initial work with the long chain esters involved testing the esters in industrial rubber belts containing polyester cords for automotive power train systems. An important part of the construction of automotive belts is the bonding of the rubber to polyester cord.

Polyester cord is used to provide strength and longevity to the belts. The polymer of choice for automotive belts is ethylene/propylene/diene polymer (EPDM). This polymer is excellent for the end use, but one of its drawbacks is poor adhesion to many substrates, such as polyester cord. Rubber companies go to great lengths to insure the proper adhesion between the EPDM and the polyester cord. At present, they use a treated cord that has a resorcinol-formaldehyde resin coating, and the resin-coated cords are then dipped in an adhesive. The resin-treated, adhesive coated cord is then bonded to the EPDM during the curing process. This is a time-consuming and expensive method to achieve rubber-to-polyester cord adhesion. The adhesion promoter systems of the invention advantageously improve adhesion of polyester cord to EPDM.

Other examples of substrates which are contemplated for use in the inventive compositions and methods include metal and polymeric layers, films, sheets, fibers, yarns and/or fabrics, including textiles, polyesters, and Aramid fibers. Metals for use in the invention include steel, brass-coated steel, brass, and copper. Adhesion to glass substrates can also be improved. Application of the adhesion promoters of the invention is particularly contemplated with steel cord, brass-coated steel cord, brass cord, polyester fiber cord, Aramid fiber cord, glass cord, fabric and flat metal surfaces, and the like. In the present application the term polymeric "cord" or "cords" is intended to include reinforcing elements used in rubber products including fibers, continuous filaments, staple, tow, yarns, fabric and the like, particularly cords for use in building the carcasses of tires such as truck tires.

The polymeric reinforcing element or cord comprises a plurality of substantially continuous fibers or monofilaments, including glass compositions, polyesters, polyamides and a number of other materials, useful in making the fibers for the reinforcing element or cords for polymeric rubber compositions and products are well known in the art. One of the preferred glasses to use is a glass known as E glass and described in "Mechanics of Pneumatic Tires," Clark, National Bureau of Standards Monograph 122, U.S. Dept. of Commerce, issued November 1971, pages 241-243, 290 and 291, incorporated herein by reference. The number of filaments or fibers employed in the fiber reinforcing element or cord can vary considerably depending on the ultimate use or service requirements. Likewise, the number of strands of fibers used to make a fiber reinforcing element or cord can vary widely. In general, the number of filaments in the fiber reinforcing element or cord for a passenger car tire can vary from about 500 to 3,000 and the number of strands in the reinforcing element can vary from 1 to 10. Preferably the number of strands is from 1 to 7 and the total number of filaments about 2,000. A representative industry glass tire cord

known as G-75 (or G-75, 5/0) has 5 strands each with 408 glass filaments. Another representative cord known as G-15 has a single strand containing 2,040 glass filaments.

The adhesive promoters of the invention can be used in numerous applications, including bonding the steel braid to the natural and/or synthetic rubber material of hoses and the metal housing of motor mounts.

The term "vulcanization" used herein means the introduction of three dimensional cross-linked structures between rubber molecules. Thus, thiuram vulcanization, peroxide vulcanization, quinoid vulcanization, resin vulcanization, metal salt vulcanization, metal oxide vulcanization, polyamine vulcanization, radiation vulcanization, hexamethylenetetramine vulcanization, urethane cross-linker vulcanization and the like are included in addition to sulfur vulcanization which is usual and most important.

Rubbers useful in the compositions described herein can be natural rubbers (NR) and/or synthetic rubbers.

Synthetic rubbers include homopolymers of conjugated diene compounds, such as isoprene, butadiene, chloroprene and the like, for example, polyisoprene rubber (IR), polybutadiene rubber (BR), polychloroprene rubber and the like; copolymers of the above described conjugated diene compounds with vinyl compounds, such as styrene, acrylonitrile, vinyl pyridine, acrylic acid, methacrylic acid, alkyl acrylates, alkyl methacrylates and the like, for example, styrene-butadiene copolymeric rubber (SBR), vinylpyridine-butadiene-styrene copolymeric rubber, acrylonitrile-butadiene copolymeric rubber, acrylic acid-butadiene copolymeric rubber, methacrylic acid-butadiene copolymeric rubber, methyl acrylate-butadiene copolymeric rubber, methyl methacrylate-butadiene copolymeric rubber, acrylonitrile-butadiene-styrene terpolymer, and the like; copolymers of olefins, such as ethylene, propylene, isobutylene and the like with dienes, for example isobutylene-isoprene copolymeric rubber (IIR); copolymers of olefins with non-conjugated dienes (EPDM), for example, ethylene-propylene-cyclopentadiene terpolymer, ethylene-propylene-5-ethylidene-2-norbornene terpolymer and ethylene-propylene-1,4-hexadiene terpolymer; polyalkenamer obtained by ring opening polymerization of cycloolefins, for example, polypentenamer; rubbers obtained by ring opening polymerization of oxirane ring, for example, polyepichlorohydrin rubber and polypropylene oxide rubber which can be vulcanized with sulfur, silicone rubbers, and the like. Furthermore, halides of the above-described various rubbers, for example, chlorinated isobutylene-isoprene copolymeric rubber (CI-IIR), brominated isobutylene-isoprene copolymeric rubber (Br-IIR), fluorinated polyethylene, and the like are included.

Particularly, the compositions described herein are characterized in that the surfaces of the vulcanized rubbers of natural rubber (NR), and synthetic rubbers, *e.g.* styrene-butadiene copolymeric rubber (SBR), polybutadiene rubber (BR), polyisoprene rubber (IR), isobutylene-isoprene, copolymeric rubber, halides of these rubbers (CI-IIR, Br-IIR) and copolymers (EPDM) of olefins with non-conjugated dienes, which are poor in the adhering ability, are improved to provide them a high adhering ability. Of course, the present invention can be applied to the other rubbers. All these rubbers may be kneaded with compounding agents conventionally used for compounding with rubber, for example, fillers, such as carbon black, silica, calcium carbonate, lignin and the like, softening agents, such as mineral oils, vegetable oils, prior to the vulcanization and then vulcanized.

The vulcanized rubbers, the surface of which has been treated with the adhesion promoter systems described herein can be easily adhered to the other materials, together with an adhesive resin, particularly metals and polymers, particularly in cord form.

In order to cure a rubber composition a vulcanizing agent such as a sulfur or peroxide vulcanizing agent is dispersed throughout the composition. The vulcanizing agent may be used in an amount ranging from 0.5 to 6.0%, based on the weight of the natural and/or synthetic rubbers in the composition, with a range of from 1.0 to 4.0% being preferred. Representative examples of sulfur vulcanizing agents include elemental sulfur (S_8), an amine disulfide, polymeric polysulfide and sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur.

Other suitable vulcanizing agents include thiuram, quinoid, metal salt, metal oxide, polyamine, vulcanization, radiation, hexamethylenetetramine, urethane cross-linker, and the like. Typical examples of peroxide vulcanizing agents include dibenzoyl peroxide and di(tertiary-butyl)peroxide.

The commonly employed carbon blacks used in conventional rubber compounding applications can be used as the carbon black in this invention. Representative examples of such carbon blacks include N110, N121, N220, N231, N234, N242, N293, N299, S315, N326, N330, M332, N339, N343, N347, N351, N358 and N375.

The rubber compositions described herein are compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable or peroxide-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, sulfur donors, curing aids, such as activators and retarders and processing additives, such as oils, resins including tackifying resins and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, retarders and peptizing

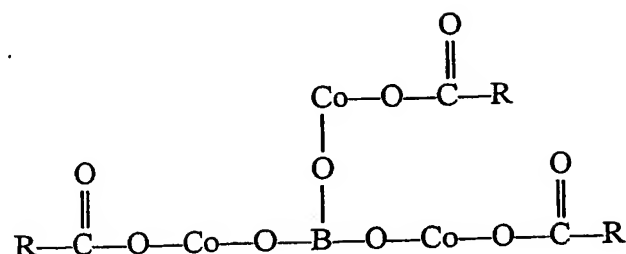
agents. As known to those skilled in the art, the additives mentioned above are selected and commonly used in conventional amounts for tire tread applications. Typical amount of adhesive resins, comprise about 0.2 to about 10%, based on the weight of natural and/or synthetic rubbers, usually about 1 to 5%.

Typical amounts of zinc oxide comprise about 2 to about 5%. Typical amounts of waxes comprise about 1 to about 5% based on the weight of natural and/or synthetic rubbers. Often microcrystalline waxes are used. Typical amounts of retarders range from 0.05 to 2%. Typical amounts of peptizers comprise about 0.1 to 1%. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide. All additive percentages are based on the weight of natural and/or synthetic rubbers.

Accelerators may be used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. The accelerator(s) may be used in total amounts ranging from about 0.5 to about 4%, preferably about 0.8 to about 1.5%, based on the weight of natural and/or synthetic rubbers. Suitable types of accelerators that may be used are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. If included in the rubber composition, the primary accelerator preferably is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

When the adhesion promoter systems containing a long chain ester and an adhesive resin are used as a wire coat or bead coat, *e.g.*, for use in a tire, the adhesion promoter system typically does not include an organo-cobalt compound, and may be used in whole or as a partial replacement for an organo-cobalt compound which serves as a wire adhesion promoter. When used in part, any of the organo-cobalt compounds known in the art to promote the adhesion of rubber to metal also may be included. Thus, suitable organo-cobalt compounds which may be employed, in combination with the non-cobalt adhesion promoter systems containing long chain esters described herein, include cobalt salts of fatty acids such as stearic, palmitic, oleic, linoleic and the like; cobalt salts of aliphatic or alicyclic carboxylic acids having from 6 to 30 carbon atoms; cobalt chloride, cobalt naphthenate; cobalt carboxylate and an organo-cobalt-boron complex commercially available under the designation Comend A from Shepherd Chemical Company, Cincinnati, Ohio.

Comend A is believed to have the structure:



wherein each R, same or different, is an alkyl group having from 9 to 12 carbon atoms, and B is a hydrocarbon chain, C₄-C₂₄, straight chain or branched, saturated or unsaturated.

Amounts of organo-cobalt compound which may be employed depend upon the specific nature of the organo-cobalt compound selected, particularly the amount of cobalt metal present in the compound. Since the amount of cobalt metal varies considerably in organo-cobalt compounds which are suitable for use, it is most appropriate and convenient to base the amount of the organo-cobalt compound utilized on the amount of cobalt metal desired in the finished composition. Accordingly, it may in general be stated that if an organo-cobalt compound is included in the rubber composition, the amount of organo-cobalt compound present in the stock composition should be sufficient to provide from about 0.01 percent to about 0.35 percent by weight of cobalt metal based upon total weight of the rubber in the composition, with the preferred amounts being from about 0.03 percent to about 0.2 percent by weight of cobalt metal based on the total weight of rubber in the composition.

The adhesion promoters described herein are especially effective in compositions in which the rubber is cis-polyisoprene, either natural or synthetic, and in blends containing at least 25% by weight of cis-polyisoprene with other rubbers. Preferably the rubber, if a blend, contains at least 40% and more preferably at least 60% by weight of cis-polyisoprene. Examples of other rubbers which may be blended with cis-polyisoprene include poly-1,3-butadiene, copolymers of 1,3-butadiene with other monomers, for example styrene, acrylonitrile, isobutylene and methyl methacrylate, ethylene/propylene/diene terpolymers, and halogen-containing rubbers such as chlorobutyl, bromobutyl and chloroprene rubbers.

The amount of sulphur in the composition is typically from 2 to 8 parts, for example from 3 to 6, by weight per 100 parts by weight of rubber, but lesser or larger amounts, for example from 1 to 7 or 8 parts on the same basis, may be employed. A preferred range is from 2.5 to 6 parts per 100 parts by weight of rubber.

Additional examples of vulcanization accelerators which can be used in the rubber compositions described herein are the thiazole-based accelerators, for example 2-

mercaptobenzothiazole, bis(2-benzothiazolyl)disulphide, 2(2',4'-dinitrophenyl-thio)benzothiazole, benzothiazole-2-sulphenamides for instance N-isopropylbenzothiazole-2-sulphenamide, N-tert-butyl-benzothiazole-2-sulphenamide, N-cyclohexylbenzothiazole-2-sulphenamide, and 2(morpholiniothio)benzothiazole, and thiocarbamylsulphenamides, for example N,N-dimethyl-N',N'-dicyclohexylthiocarbamoyl-sulphenamide and N(morpholiniothiocarbonylthio)-morpholine. A single accelerator or a mixture of accelerators may be used. In the compositions described herein, these vulcanization accelerators are usually used in amounts of from 0.3 to 2, for example from 0.3 to 1.5, preferably from 0.4 to 1.0 and more preferably from 0.5 to 0.8, parts by weight per 100 parts by weight of rubber.

The adhesion promoters described herein are very effective in promoting bonding between rubber and brass, for example the bonding between rubber and brass-coated steel. The brass typically has a copper content of from 60 to 70% by weight, more especially from 63 to 68% by weight, with the optimum percentage depending on the particular conditions under which the bond is formed. The brass coating on brass-coated steel can have a thickness of, for example, from 0.05 to 1 micrometer, preferably from 0.07 to 0.7 micrometer, for example from 0.15 to 0.4 micrometer.

The long chain ester additive/resin combinations (*i.e.*, adhesion promoter systems) described herein are particularly useful to adhere rubber to steel cord, where conventional adhesive pretreatment has been largely ineffective. Rubber can also be bonded effectively to alloys of copper and zinc containing small amounts of one or more other metals, for example cobalt, nickel or iron.

For bonding rubber to zinc, as for example in bonding rubber to zinc-coated steel cords (which are widely used in the manufacture of conveyor belting) cobalt compounds have been used as adhesion promoters. Examples of such compounds are cobalt naphthenate and the cobalt-boron complexes described in GB 2 022 089 A.

Vulcanization of the rubber composition described herein is generally carried out at conventional temperatures ranging from about 100°C. to 200°C. Preferably, the vulcanization is conducted at temperatures ranging from about 110°C. to 180°C. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

Upon vulcanization of the rubber composition at a temperature ranging from 100°C. to 200°C., the rubber composition can be used for various purposes. For example, the vulcanized rubber composition may be in the form of a tire, belt, hose, motor mounts, gaskets and air springs. In the case of a tire, it can be used for various tire components. Such tires

can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art. When the rubber composition is used in a tire, its use may be in a wire coat, bead coat, tread, apex, sidewall and combination thereof. As can be appreciated, the tire may be a passenger tire, aircraft tire, truck tire, and the like. Preferably, the tire is a passenger tire. The tire may also be a radial or bias, with a radial tire being preferred.

The invention may be better understood by reference to the following examples in which parts and percentages are by weight unless otherwise indicated.

In Part I of this project, compounds were mixed into existing EPDM recipes and tested for adhesion. The following varieties were tested:

Variable	Example 1	Example 2	Example 3	Example 4	Example 5
	Cyrez® CRA- 133M	Cyrez® CRA- 148M	Control- Current EPDM Formula	Cyrez® CRA- 133M/ RX-13804	Cyrez® CRA- 148M/ RX-13804

Cyrez® CRA-133M - Melamine-formaldehyde resin with 27% calcium silicate

Cyrez® CRA-148M - Melamine-formaldehyde resin with 27% calcium silicate

RX-13804 = Di-2-ethylhexyl dimerate (EMPOL 1016 dimer acid esterified with 2-ethylhexyl alcohol, containing predominantly C₃₆ dimer acids and C₅₄ trimer acids, containing both saturated and unsaturated long chain (C₆-C₁₈) radicals with 0, 1, 2, and/or 3 carbon-to-carbon double bonds.

The melamine-formaldehyde resins are known as adhesion promoters in the tire industry. The need for rubber-to-cord adhesion generally requires the presence of a methylene donor/methylene acceptor resin system, as described above. The typical system consists of hexakismethoxymethylmelamine (HMMM) as the donor and a Novolak resin (such as resorcinol) as the acceptor.

Results

The table below shows adhesion results with polyester cord in Examples 1-5.

Compound Variable	Adhesion-lbs-force	
	Room Temperature	257°C
Example 1: (Cyrez® CRA-133M)	23.48	2.91
Example 2: (Cyrez® CRA-148M)	21.57	3.58
Example 3: (Control)	22.21	4.88
Example 4: (Cyrez® CRA-133M / RX-13804)	48.76	10.21
Example 5: (Cyrez® CRA-148M / RX-13804)	47.70	14.21

The control (Example 3) was EPDM with the polyester cord pretreated with a melamine formaldehyde resin and an adhesive from Lord Corporation (Cary, North Carolina). The polyester cord used in Examples 1, 2, 4, and 5 were treated with melamine formaldehyde resin but not with an adhesive. Examples 1 and 2 contain just the melamine resin and provide basically equal adhesion to the control compound, which is significant since the cords used were not coated with adhesive. Examples 4 and 5 contain a combination of resin and the esters described herein, and show an unexpected increase in adhesion. The adhesive forces for Examples 4 and 5 are increased at least 100% compared to the control and resin only Examples (1-3).

These results indicate that the resin/ester combination provides a dramatic increase in adhesive force between EPDM and polyester cord compared to the control compound and the compounds containing only resin.

The formulation and data collected for Examples 1-5 are shown in Table I:

TABLE I







	Example 1	Example 2	Example 3	Example 4	Example 5
Nordel IP3720 (EPDM)	100.00				
N762 Carbon Black	56.00				
Kadox 930 Zinc Oxide	5.00				
Ricon 150	5.00				
SR350	4.00				
Cyrez® CRA-133M	7.00	-	-	7.00	-
Cyrez® CRA-148M	-	7.00	-	-	7.00
RX-13804	-	-	-	10.00	10.00
Subtotal	177.00	177.00	170.00	187.00	187.00
<u>MILL ADDITION</u>					
Vulcup 40KE	7.00				
Total	184.00	184.00	177.00	194.00	194.00

TABLE I - (CONT)

Major Variable	Cyrez® CRA-133M	Cyrez® CRA-148M	Control	Cyrez® CRA-133M/ RX-13804	Cyrez® CRA-148M/ RX-13804
	Example 1	Example 2	Example 3	Example 4	Example 5

Viscosity and Curing PropertiesMooney Viscosity at 212°F

Minimum Viscosity
t5, minutes

41.3	41.9	41.8	30.3	33.9
			56.8	

Mooney Viscosity at 250°F

Minimum Viscosity
t5, minutes
t10, minutes
t35, minutes

31	32.7	34.9	25.9	28.5
10.8	11.1	9.7	8.3	8.3
11.8	12.8	11.3	9.3	9
13.8	18.3	17		11.8

Oscillating Disc Rheometer at

350°F

M_LM_Ht₃₂, minutest_c(90), minutes1.25*t_c(90), minutes

Cure Rate Index

19	9	8.3	6.3	8.8
151.9	159.3	156.6	57.8	62.9
0.92	0.92	0.83	0.92	1.2
7.5	7.2	7.9	5.7	6.3
9.4	9	9.9	7.1	7.8
15.2	16	14.1	21.1	19.7

TABLE I - (CONT)

Major Variable	Cyrez® CRA-133M	Cyrez® CRA-148M	Control	Cyrez® CRA-133M/ RX-13804	Cyrez® CRA-148M/ RX-13804
	Example 1	Example 2	Example 3	Example 4	Example 5
Note: Cpd 4 & 5 Stuck To Rheometer & Press Mold					
<u>Original Physical Properties</u>					
Stress @ 100% Elongation, MPa	13.1	14.1	15.2	4.7	4.9
psi	1905	2050	2200	680	705
Stress @ 200% Elongation, MPa				9.9	9.5
Stress @ 300% Elongation, MPa					
Tensile Ultimate, MPa	19.0	18.1	18.7	12.5	10.9
psi	2760	2625	2705	1815	1580
Elongation @ Break, %	135	120	115	250	235
Hardness Duro A, pts.	83	83	80	78	75
Specific Gravity	1.1043	1.1085	1.1061	1.1075	1.1081

Adhesion Promoter

PART II

Based on Part I results which show improved adhesion of EPDM rubber to polyester cord, the resin/ester combination was evaluated in a standard natural rubber compound used for metal cord adhesion.

The compounds tested in this study were varied in ester content, with resin content kept constant. The following Table II lists the adhesion results for original, air oven aging, and humidity aging, in Examples 6-12, with parts by weight of resin and ester set forth in parentheses.

TABLE II

Recipe Variable	Standard Resorcinol (3.85)/melamine formaldehyde (4.23)	Cyrez® CRA-148M	Cyrez® CRA-148M(8)/SM RX-13804(8)	Cyrez® CRA-148M(8)/SM RX-13804(6)	Cyrez® CRA-148M(8)/SM RX-13804(4)	Cyrez® CRA-148M(8)/SM RX-13804(2)	Cyrez® CRA-148M(8)/SM RX-13804(6)/Sulfur(8.4)/Vulkacit (0.75)
	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Adhesion to Steel Cord							
Original Properties:							
Max. Force, lbs. (avg.)		156	162.7	162.6	138.6	167.4	162
Average	176.2	95	100	100	100	99	100
Coverage, %	100						
Air Oven Aging: 48 hrs. @ 121°C (250°F)							
Max. Force, lbs. (avg.)		73.5	68.9	76.8	77.6	87.7	123
Average	105.6	93	97	97	99	95	95
Coverage, %	99	-53	-58	-57	-44	-48	-24
Force Change, %	-40						

TABLE II (CONT.)

Recipe Variable	Standard Resorcinol (3.85)/melamine formaldehyde (4.23)	Cyrez® CRA-148M	Cyrez® CRA-148M(8)/SM RX-13804(8)	Cyrez® CRA-148M(8)/SM RX-13804(6)	Cyrez® CRA-148M(8)/SM RX-13804(4)	Cyrez® CRA-148M(8)/SM RX-13804(2)	Cyrez® CRA-148M(8)/SM RX-13804(6)/Sulfur(8.4)/Vulkacit (0.75)
	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Adhesion to Steel Cord Humidity Aging: 7 Days @ 94°C (200°F)							
Max. Force, lbs. (avg.)	152.3	119.7	130.4	160.3	137.7	136.9	152.7
Average Coverage, %	100	98	100	100	100	100	99
Force Change, %	-14	-23	-20	-1.4	-0.65	-18	-5.7
Humidity Aging: 14 Days @ 94°C (200°F)							
Max. Force, lbs. (avg.)	123.7	94.9	130.2	115.3	116.8	125.3	148.6
Average Coverage, %	88	75	93	90	90	90	95
Force Change, %	-30	-39	-20	-29	-16	-25	-8.3

TABLE II (CONT.)

Recipe Variable	Standard Resorcinol (3.85)/melamine formaldehyde (4.23)	Cyrez® CRA- 148M	Cyrez® CRA- 148M(8)/SM RX-13804(8)	Cyrez® CRA- 148M(8)/SM RX-13804(6)	Cyrez® CRA- 148M(8)/SM RX-13804(4)	Cyrez® CRA- 148M(8)/SM RX-13804(2)	Cyrez® CRA-148 M(8)/SM RX-13804(6)/ Sulfur(8.4)/Vulkacit (0.75)
	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Humidity Aging: 21 Days @ 94°C (200°F)							
Max. Force, lbs. (avg.)	101.4	64.4	82.6	107.9	90.3	108.1	127.3
Average							
Coverage, %	87	75	70	77	83	83	93
Force Change, %	-43	-59	-49	-34	-35	-35	-21

The original wire cord adhesion results show the standard formulation to have slightly higher adhesion than formulations containing resin/ester combinations. The formulations containing resin/ester combinations are all very similar except for the resin/ester combination of 8/4. At this time, the reason why this formulation has poorer original adhesion is not known.

The humidity aging results are interesting in that Examples 9, 11 and 12 have the highest force levels and lowest percent change from the original. Example 12 has a 50% increase in curing agent amount to offset the addition of ester to the compound. This formulation had the highest force recorded and the least change from the original adhesion. This suggests that an increase in the amount of curing agent can, along with the resin/ester combination, improve aged adhesion. All the resin/ester compounds except for Example 8 (resin 8/ester 8) exhibited lower changes in recorded force than the standard compound.

The formulation for Examples 6-12 are shown in Table III.

TABLE III

	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
SMR-L	100.00						
N326	60.00						
Kadox 930	10.00						
Cobalt Naphthenate	2.00						
Stearic Acid	1.20						
Santoflex 13	1.00						
PVI	0.20						
Pennacolite (3.85)/Resimene (4.23)	8.08	--	--	--	--	--	--
Cyrez® CRA-148M	--	8.08	8.00	8.00	8.00	8.00	8.00
SM RX-13804	--	--	8.00	6.00	4.00	2.00	6.00
Subtotal	182.48	182.48	190.40	188.40	186.40	184.40	188.40
Mill Addition							
Sulfur	5.60						8.40
Vulkacit DZ	0.50						0.75
Total	188.58	188.58	196.50	194.50	192.50	190.50	197.55

TABLE III (CONT.)

Major Variable	Pennacolite (3.85)/ Resimene (4.23)	Cyrez® CRA- 148M	Cyrez® CRA- 148M(8)/SM RX-13804(8)	Cyrez® CRA- 148M(8)/SM RX-13804(6)	Cyrez® CRA- 148M(8)/SM RX-13804(4)	Cyrez® CRA- 148M(8)/SM RX-13804(2)	Cyrez® CRA-148 M(8)/SM RX-13804(6)/ Sulfur(8.4)/Vulkacit (0.75)
	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Viscosity and Curing Properties							
Mooney Viscosity @ 168°C (335°F)	70.2	67.9	57.9	59.7	62.1	63.7	48.1
Min. Viscosity	1.4	1.8	1.9	1.8	2.2	2	1.7
t ₅ , minutes	1.8	2	2.2	2.2	2.5	2.3	2
t ₁₀ , minutes	2.9	2.6	2.8	2.8	3.3	2.9	2.6
t ₃₅ , minutes							
Oscillating Disc Rheometer at 168°C (335°F)							
M _L	16.6	16.9	14.1	14.8	15.7	15.8	16
M _H	47.5	26.6	23.6	24.6	22.2	38.8	73.6
t ₂ , minutes	1.4	1.8	1.8	1.8	1.8	1.8	1.6
t _c (90), minutes	5.3	4.5	4.7	4.7	4.4	4.9	5.3
1.25*t _c (90), minutes	6.7	5.6	5.8	5.8	5.5	6.2	6.7
Cure Rate Index	25.6	36.4	35.2	35.2	37.5	31.6	26.7

TABLE III (CONT.)

Major Variable	Pennacolite (3.85)/ Resimene (4.23)	Cyrez® CRA- 148M	Cyrez® CRA- 148M(8)/SM RX-13804(8)	Cyrez® CRA- 148M(8)/SM RX-13804(6)	Cyrez® CRA- 148M(8)/SM RX-13804(4)	Cyrez® CRA- 148M(8)/SM RX-13804(2)	Cyrez® CRA-148 M(8)/SM RX-13804(6)/ Sulfur(8.4)/Vulkacit (0.75)
	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Original Physical Properties							
Stress @ 100% Elongation, MPa	7.0	5.9	3.9	5.1	5.0	5.8	7.6
psi	1010	855	565	740	730	845	1105
Stress @ 200% Elongation, MPa	14.8	12.4	8.8	10.9	10.8	12.1	14.8
Stress @ 300% Elongation, MPa	--	19.2	14.8	17.1	16.9	18.6	--
Tensile Ultimate, MPa	20.4	20.9	21.5	20.6	21.2	20.7	20.1
psi	2960	3025	3116	2990	3080	3010	2915
Elongation @ Break, %	275	330	415	370	380	335	285
Hardness Duro A, pts.	79	78	72	75	76	77	79
Specific Gravity	AVERAGE	1.204	AVERAGE	AVERAGE	AVERAGE	--	1.203

The use of the resin/ester combination in a sulfur-cured natural rubber formulation can improve wire cord adhesion after heat aging and humidity aging as compared to a standard natural rubber formulation.

In order to verify that the increased cure system of Example 12 was not solely responsible for the increased adhesion performance of Example 12, an additional formulation, Example 13, was tested. The only difference between Examples 6 and 13 is that Example 13 has a 50% increase in the amount of cure system additives (Sulfur and Vulkacit). Table IV provides comparative data which demonstrates that increasing the cure system of the "control compound" (*i.e.*, the prior art formulation of Example 6) by 50% does not lead to an increased adhesive effect. Accordingly, these data confirm that the increase in adhesion observed in Example 12 cannot solely be attributed to the increased amount of cure system additives, *i.e.*, the increased adhesion is due to the adhesion promoter.

TABLE IV

Recipe Variable	Pennacolite (3.85)/ Resimene (4.23)/ Sulfur (8.4)/ Vulkacit (0.75)	Pennacolite (3.85)/ Resimene (4.23) "Control"	Cyrez® CRA- 148M(8)/ SM RX- 13804(6)/ Sulfur (8.4)/ Vulkacit (0.75)
	Example 13	Example 6	Example 12
SMR-L	100	→	→
N 326	60	→	→
Kadox 930	10	→	→
Cobalt Napthenate	2	→	→
Stearic Acid	1.20	→	→
Santoflex 13	1.00	→	→
PVI	0.20	→	→
Pennacolite (3.85)/ Resimene (4.23)	8.08	8.08	---
Cyrez® CRA-148M	---	---	8.00
SM RX-13804	---	---	6.00
Subtotal	182.48	182.48	188.40
Mill Addition			
Sulfur	8.40	5.60	8.40
Vulkacit	0.75	0.50	0.75
Total	191.63	188.58	197.55

TABLE IV (CONT.)

Major Variable	Pennacolite (3.85)/ Resimene (4.23)/ Sulfur (8.4)/ Vulkacit (0.75)	Pennacolite (3.85)/ Resimene (4.23) "Control"	Cyrez® CRA- 148M(8)/ SM RX- 13804(6)/ Sulfur (8.4)/ Vulkacit (0.75)
Processing Properties	Example 13	Example 6	Example 12
Viscosity and Curing Properties			
Mooney Viscosity at 168°C (335°F)			
Minimum Viscosity	69.3	77.2	66.4
t ₅ , minutes	1.3	1.2	1.3
t ₁₀ , minutes	1.6	1.3	1.6
t ₃₅ , minutes	2.3	1.9	2.2
Oscillating Disc Rheometer at 168°C (335°F)			
M _L	17	20	17.3
M _H	100.5	101.1	88.4
t ₂ , minutes	1.4	1.5	1.7
t'c(90), minutes	6.7	9.6	5.9
1.25*t'c(90), mins.	8.3	12	7.4
Cure Rate Index	19.1	12.4	23.5
Vulcanizate Properties			
Original Physical Properties			
Stress @ 100% Elongation, MPa	8.1	6.5	5.9
psi	1170	945	850
Stress @ 200% Elongation, MPa	15.7	13.7	11.5
Stress @ 300% Elongation, MPa	—	—	16.9
Tensile Ultimate, MPa	18.4	20.1	18.7
psi	2665	2920	2710
Elongation @ Break, %	240	300	330
Hardness Duro A, pts.	82	80	80
Specific Gravity	1.201	1.199	1.204
Adhesion to Steel Cord			
Original Properties:			
Max. Force, lbs. (avg.)			
Set 1	90.1	104.4	80.3
Set 2	78.4	99.3	80.6
Set 3	82.4	101.1	103.3
Average	83.6	101.6	88.1
Coverage, %	90	90	90

Adhesion Promoter**Part III**

Next, natural rubber-to-metal bonding was evaluated to determine the effect of added ester(s), as described herein. This presents a large potential for automotive parts, such as motor mounts, brakes, hoses, and the like.

The first study focused on long chain esters in natural rubber and their effect on adhesion to metal (see Table V - Examples 14-17). The data indicate that the adhesion promoters described herein improve adhesion to brass in a sulfur-cured rubber formulation. The use of the resin/ester combination did not improve adhesion versus compounds with ester only.

TABLE V

	Example 14	Example 15	Example 16	Example 17
SMR-L	100.00	→		
Kadox 930	5.00	→		
Stearic Acid	2.00	→		
N 330	35.00	→		
Cyrez® CRA-148M	6.95	--	6.95	--
RX-13804	6.95	5.00	6.95	--
Subtotal	155.90	147.00	155.90	142.00
Mill Addition				
Sulfur	2.25	--	--	--
Santocure TBSI	0.70	--	--	--
DiCup 40KE	--	5.00	→	
Total	158.85	152.00	160.90	147.00

TABLE V (CONT.)

Major Variable	RX-13804/Cyrez® CRA-148M	RX-13804	RX-13804/Cyrez® CRA-148M	Control
	Example 14	Example 15	Example 16	Example 17
Viscosity and Curing Properties				
Mooney Viscosity at 335°F (168°C)				
Minimum Viscosity	47.5	46.5	62	56
t ₅ , minutes	2	1.1	0.75	0.85
t ₁₀ , minutes	2.3	1.3	0.85	1
t ₃₅ , minutes	3	1.7	1.1	1.8
Oscillating Disc Rheometer at 335°F (168°C)				
M _L	13.4	12.4	11.4	13.1
M _H	41.9	67	74.2	74.6
t ₂ , minutes	1.8	1.3	1.2	1.1
t' _c (90), minutes	7.2	13.6	15.3	14.5
1.25*t' _c (90), minutes	9	17	19.1	18.1
Cure Rate Index	18.7	8.1	7.1	7.5
Original Physical Properties				
Stress @ 100% Elongation, MPa	2.0	4.0	5.5	5.1
psi	290	575	800	735
Stress @ 200% Elongation, MPa	5.6	14.7	--	--
Stress @ 300% Elongation, MPa	10.6	--	--	--
Tensile Ultimate MPa	16.5	16.4	9.9	16.2
psi	2390	2385	1440	2355
Elongation @ Break, %	440	215	140	190
Hardness Duro A, pts.	52	57	62	61
Specific Gravity	1.097	1.082	1.105	1.090

TABLE V (CONT.)

Major Variable	RX-13804/Cyrez® CRA-148M	RX-13804	RX-13804/Cyrez® CRA-148M	Control
	Example 14	Example 15	Example 16	Example 17
Metal Adhesion- ASTM D429	Sulfur	Peroxide	Peroxide	Peroxide
Brass				
Adhesion Force, lbf/in. width	82.58	1.69	--	--
Failure Type	R	R	R	R
% Failure	100	100	100	100
Aluminum				
Adhesion Force, lbf/in. width	--	--	--	--
Failure Type	R	R	R	R
% Failure	100	100	100	100
Steel				
Adhesion Force, lbf/in. width	--	--	--	--
Failure Type	R	R	R	R
% Failure	100	100	100	100

R = rubber failure, RC = rubber-cement failure, CP = cement-primer failure,
M = primer-metal failure
Compounds 2, 3 and 4 bloomed.

Table VI provides data wherein a sulfur cure system was used in formulations containing resin only (Example 18), a resin combined with a long chain ester of the disclosure (Example 20), and a control containing no resin and no ester (Example 19). From these data, it can be seen that the adhesion promoter system including a long chain ester and an adhesive resin performs best, and gives superior adhesive results when compared with the control formulation and the formulation containing the resin, but not including an ester of the disclosure.

TABLE VI

Recipe Variable	Cyrez® CRA Resin 148M	"Control"	Cyrez® CRA Resin 148M/ RX 13804
	Example 18	Example 19	Example 20
SMR-L	100		
Kadox 930	5.00		
Stearic Acid	2.00		
N 330	35.00		
Cyrez® Resin 148M	7.00	---	7.00
RX-13804	---	---	7.00
Subtotal	149.00	142.00	156.00
Mill Addition			
Sulfur	2.25	2.25	2.25
Santocure TBSI	0.70	0.70	0.70
Total	151.95	144.95	158.95

TABLE VI (CONT.)

Recipe Variable	Cyrez® CRA Resin 148M	"Control"	Cyrez® CRA Resin 148M/ RX-13804
	Example 18	Example 19	Example 20
Viscosity and Curing Properties			
Mooney Viscosity at 168°C (335°F)			
Minimum Viscosity	48.1	53.2	48.2
t ₅ , minutes	2.1	1.5	2
t ₁₀ , minutes	2.4	1.8	2.3
t ₃₅ , minutes	3.2	2.6	2.9
Oscillating Disc Rheometer at 168°C (335°F)			
M _L	13.7	14.6	13.5
M _H	31.2	36	40.9
t ₂ , minutes	1.8	1.7	1.8
t' _c (90), minutes	5.3	5.3	7.1
1.25*t' _c (90), minutes	6.7	6.7	9
Cure Rate Index	28.6	27.3	19
Vulcanizate Properties			
Original Physical Properties			
Stress @ 100% Elongation, MPa	1.9	1.8	2.0
psi	280	255	300
Stress @ 200% Elongation, MPa	4.7	4.5	5.6
Stress @ 300% Elongation, MPa	8.6	8.8	10.6
Tensile Ultimate MPa	22.1	24.5	16.5
psi	3205	3560	2380
Elongation @ Break, %	555	565	440
Hardness Duro A, pts.	57	55	52
Specific Gravity	--	--	1.097

TABLE VI (CONT.)

Recipe Variable	Cyrez® CRA Resin 148M	"Control"	Cyrez® CRA Resin 148M/ RX-13804
	Example 18	Example 19	Example 20
Metal Adhesion - ASTM D249			
Brass			
Adhesion Force, lbf/in. width	118.2	46.3	138.9
Failure Type	R, RM	R	R, RM
% Failure	95, 5	100	95, 5
Aluminum			
Adhesion Force, lbf/in. width	Fail	Fail	Fail
Failure Type	RM	RM	RM
% Failure	100	100	100
Steel			
Adhesion Force, lbf/in. width	Fail	Fail	Fail
Failure Type	RM	RM	RM
% Failure	100	100	100

R = rubber failure, RC = rubber-cement failure, CP = cement-primer failure,
M = primer-metal failure, RM = rubber metal failure

Next, the effect of the long chain esters described herein was evaluated in an EPDM rubber formulation for rubber to metal bonding. The cure system was also evaluated to determine the effect of peroxide versus a sulfur system. The sulfur formulations did not work, thus these formulations were discarded. The peroxide cured formulations were varied by using the ester alone and the resin/ester combination. The data below in Table VII (Examples 21-23), lists adhesion results for brass, aluminum and steel cord in EPDM.

TABLE VII

Major Variable	RX-13804	RX-13804/Cyrez® CRA-148M	Control
	Example 21	Example 22	Example 23
Brass			
Adhesion Force, lbf/in. width	1.26	52.43	--
Failure Type	R	R	R
% Failure	100	100	100
Aluminum			
Adhesion Force, lbf/in. width	--	--	--
Failure Type	R	R	R
% Failure	100	100	100
Steel			
Adhesion Force, lbf/in. width	16.82	19.97	--
Failure Type	R	R	R
% Failure	100	100	100

R = rubber failure, RC = rubber-cement failure, CP = cement-primer failure,
M = primer-metal failure

The formulation containing the resin/ester has significantly greater adhesion to brass than the formulation with just ester, and the control. The steel adhesion results show that the formulation with ester does provide some adhesion, but the resin/ester combination is unexpectedly better. The control formulation has no adhesion to steel. None of the formulations has adhesion to aluminum.

The recipe/formulation data for Examples 21-23 is shown in Table VIII:

TABLE VIII

	Example 21	Example 22	Example 23
Nordel IP 3720	100		
N762	56		
Kadox 930	5.00		
Ricon 150	5.00		
SR 350	4.00		
RX-13804	10.00	7.00	--
Cyrez® Resin 148M	--	10.00	--
Subtotal	180.00	187.00	170.00
Mill Addition			
VulCup 40KE	7.00		
Total	187.00	194.00	177.00

TABLE VIII (CONT.)

Major Variable	RX-13804	RX-13804/Cyrez® CRA-148M	Control
	Example 21	Example 22	Example 23
	Peroxide Cure		
Viscosity and Curing Properties			
Mooney Viscosity at 168°C (335°F)			
Minimum Viscosity	23.9	29.6	33.6
t ₅ , minutes	9.5	11.2	7.5
t ₁₀ , minutes	10.7	11.9	7.9
t ₃₅ , minutes	--	15.8	8.8
Oscillating Disc Rheometer at 168°C (335°F)			
M _L	6.6	12.2	9.2
M _H	87.1	92.4	177
t ₂ , minutes	0.92	0.92	0.83
t _c (90), minutes	6.5	8.4	8.5
1.25*t _c (90), minutes	8.1	10.5	10.6
Cure Rate Index	17.9	13.3	13
Original Physical Properties			
Stress @ 100% Elongation, MPa	1.4	6.5	13.7
psi	198	940	1990
Stress @ 200% Elongation, MPa	11.2	12	--
Stress @ 300% Elongation, MPa	--	--	--
Tensile Ultimate MPa	12.2	13.0	19.7
psi	1770	1890	2860
Elongation @ Break, %	200	210	135
Hardness Duro A, pts.	80	83	86
Specific Gravity	1.099887	1.122098	1.114178

Table IX provides comparative data that supplements the data presented in Table VIII. Example 24, contains resin, but does not contain any of the long chain esters disclosed

herein. As can be seen from the data of Table IX, Example 24 did not promote adhesion between EPDM and metal substrates.

Table IX also contains formulations wherein the ester was varied. A saturated ester, UBS 020602, in accordance with the disclosure, was used to formulate Examples 25 and 26. In Example 25, the saturated ester additive was not combined with an adhesive resin as described herein, and failed to promote adhesion between EPDM and the metal substrates. However, in Example 26, the saturated ester was combined with an adhesive resin, and excellent adhesion between metal substrates and EPDM, more particularly between steel and EPDM, was obtained.

TABLE IX

Recipe Variable	RX-13804/Cyrez® CRA-148M Example 22	Cyrez® CRA-148M Example 24	UBS 020602 Example 25	UBS 020602/ Cyrez® CRA-148M Example 26	Control Example 23
Nordel IP 3720	100.00				
N 762	56.00				
Kadox 930	5.00				
Ricon 150	5.00				
SR 350	4.00				
RX 13804	7.00	--	--	--	--
Cyrez® Resin 148M	10.00	10.00	--	10.00	--
UBS 020602	--	--	7.00	7.00	--
Subtotal	187.00	180.00	177.00	187.00	170.00
Mill Addition					
Vulcup 40 KE	7.00				
Total	194.00	187.00	184.00	194.00	177.00

TABLE IX (CONT.)

Recipe Variable	RX-13804/148M	Cyrez® CRA-148M	UBS 020602	UBS 020602 Cyrez® CRA-148M	Control
Processing Properties	Example 22	Example 24	Example 25	Example 26	Example 23
Viscosity and Curing Properties					
Mooney Viscosity at 121°C (250°F)					
Minimum Viscosity					
t ₅ , minutes	26.3	32.6	23.4	26.6	28.7
t ₁₀ , minutes	12.8	9.8	11.4	11.1	9.7
t ₃₅ , minutes	14.2	10.4	12.3	11.8	10.2
	FAIL	12.7	17.8	14.8	11.4
Oscillating Disc Rheometer at 177°C (350°F)					
M _L	6.7	10.8	6.7	8	8.8
M _H	74.1	115.9	129	87.4	171.6
t ₂ , minutes	0.92	0.92	1.1	1	1
t _c (90), minutes	7.4	10.1	9.1	9.3	10.3
1.25*t _c (90), minutes	9.3	12.6	11.4	11.6	12.9
Cure Rate Index	15.4	10.9	12.5	12.1	10.7
Vulcanizate Properties					
Original Physical Properties					
Stress @ 100% Elongation, MPa	6.1	9.3	8.4	6.3	13.4
psi	890	1350	1220	920	1945
Stress @ 200% Elongation, MPa	11.7	--	--	--	--

TABLE IX (CONT.)

Recipe Variable	RX-13804/148M	Cyrez® CRA-148M	UBS 020602	UBS 020602 Cyrez® CRA-148M	Control
Processing Properties	Example 22	Example 24	Example 25	Example 26	Example 23
Stress @ 300% Elongation, MPa	--	--	--	--	--
Tensile Ultimate, MPa	12.3	15.2	14.1	12.0	18.2
psi	1785	2200	2045	1735	2635
Elongation @ Break, %	205	160	145	180	125
Hardness Duro A, pts.	85	87	85	83	87
Specific Gravity	1.119	1.128	1.102	1.120	1.110
Metal Adhesion - ASTM D429					
Brass					
Adhesion Force, lbf/in. width	91	61.5	FAIL	77.6	FAIL
Failure Type	R	R	RM	R	RM
% Failure	100	100	100	100	100
Aluminum					
Adhesion Force, lbf/in. width	FAIL	FAIL	FAIL	FAIL	FAIL
Failure Type	RM	RM	RM	RM	RM
% Failure	100	100	100	100	100

TABLE IX (CONT.)

Recipe Variable	RX-13804/148M Example 22	Cyrez® CRA-148M Example 24	UBS 020602 Example 25	UBS 020602 Cyrez® CRA-148M Example 26	Control Example 23
Steel					
Adhesion Force, lb/in. width	FAIL	35.3	FAIL	77	FAIL
Failure Type	R	RM	RM	RM-R	RM
% Failure	100	100	100	67%, 33%	100

R = rubber failure, RC = rubber-cement failure, CP = cement-primer failure, M = primer-metal failure, RM = rubber metal failure

EPDM Rubber to Metal Bonding

Additional esters were evaluated to determine their effect on adhesion when combined with an adhesive resin. The esters evaluated were as follows:

Plasthall DOS	A saturated diester based on 2-ethylhexyl alcohol and sebacic acid.
RX-13577	An unsaturated monoester based on tridecyl alcohol and tall oil fatty acid.
RX-13824	An unsaturated dimerate ester based on tridecyl alcohol and a C-36 dimer acid. This ester is similar to RX-13804, which uses the same dimer acid, but RX-13804 is reacted with 2-ethylhexyl alcohol (di-2-ethylhexyl dimerate).

The results indicate that the compound with DOS/resin provides good adhesion to brass and steel. The RX-13577/resin compound has excellent adhesion to brass and steel, and the force values for steel are greater than any of the other ester/resin combinations. The data suggests that a greater degree of ester unsaturation levels provides greater adhesion because RX-13577 does have more unsaturated sites by weight than RX-13804 or RX-13824. Another piece of data that helps support the above statement is the steel adhesion data for the ester only compounds. The RX-13577 compound had the only measurable adhesion while DOS and RX-13824 had no adhesion values.

The data is set forth in Table X, Examples 27-34:

TABLE X

	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34
Nordel IP 3720	100.00							
N762	56.00							
Kadox 930	5.00							
Ricon 150	5.00							
SR 350	4.00							
Plasthall DOS	10.00	7.0						
Cyrez® CRA-148M		10.00	7.00		10.00		10.00	
RX-13577				10.00	7.00			
RX-13824						10.00	7.00	
Control								
Subtotal	180.00	187.00	177.00	180.00	187.00	180.00	187.00	170.00
Mill Addition	7.00							
Vulcup 40KE								
TOTAL	187.00	194.00	184.00	187.00	194.00	187.00	194.00	177.00

TABLE X (CONT.)

Major Variable	Plasthall DOS (dioctylsebacate)	Plasthall DOS/Cyrez® CRA-148M	Cyrez® CRA- 148M	RX-13577	RX-13577/ Cyrez® CRA- 148M	RX-13824	RX-13824/ Cyrez® CRA- 148M	Control
	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34
Plasticizer								
Processing Properties								
Viscosity and Curing Properties								
Mooney Viscosity at 250°F (121°C)								
Min. Viscosity t5, minutes	19.9	26.1	32.2	21.1	26.1	21.3	26.8	30.9
t10, minutes	8.6	9.6	8.4	7.6	7.3	8.9	7.8	6.6
t35, minutes	9.3	11.8	8.9	8.6	7.9	9.8	8.3	6.9
	FAIL	FAIL	17.6	FAIL	FAIL	FAIL	10.2	8.3
Oscillating Disc Rheometer at 350°F (177°C)								
M _L	5.5	6.6	10	6.6	7.2	6.4	8.6	9.7
M _H	88.6	63.1	84.9	58.8	52.8	75.3	58.5	125.8
t ₂ , minutes	0.92	0.92	0.92	1.3	0.92	1	0.92	0.83
t _c (90), mins	6.3	6	6.1	6.9	6	6.1	5.9	6.3
1.25*t _c (90), mins.	7.8	7.5	7.6	8.7	7.5	7.6	7.4	7.8

TABLE X (CONT.)

Major Variable	Plasthall DOS (dioctylsebacate)	Plasthall DOS/Cyrez® CRA-148M	Cyrez® CRA- 148M	RX-13577	RX-13577/ Cyrez® CRA- 148M	RX-13824	RX-13824/ Cyrez® CRA- 148M	Control
	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34
Oscillating Disc Rheometer at 350°F (177°C) (Cont)	18.8	19.7	19.4	17.6	19.7	19.7	20	18.5
Cure Rate Index								
Original Phys. Properties								
Stress @ 100% Elongation, MPa	4.8	5.0	6.4	3.8	4.5	4.2	4.7	8.2
psi	700	725	925	545	655	615	680	1195
Stress @ 200% Elongation, MPa	11.4	9.4	12.3	7.5	7.8	9.7	8.2	—
Stress @ 300% Elongation, MPa	—	—	—	11.1	10.4	—	—	—
Tensile Ultimate, MPa	13.5	11.1	13.9	12.7	10.4	11.7	10.4	18.1
psi	1960	1650	2010	1835	1515	1690	1515	2620
Elongation @ Break, %	220	250	225	320	300	235	275	175
Hardness Duro A, pts.	81	84	86	79	82	80	82	85
Specific Gravity	1.102	1.123	1.125	1.098	1.118	1.098	1.121	1.113

TABLE X (CONT.)

	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34
Metal Adhesion - ASTM D429								
Brass								
Adhesion force, lbf/in. width	--	128.1	51.1	--	139.4	--	133.5	--
Failure Type	RM	RM	R	RM	R	RM	R	RM
% Failure	100	100	100	100	100	100	100	100
Aluminum								
Adhesion force, lbf/in. width	--	--	--	--	--	--	--	--
Failure Type	RM	RM	RM	RM	RM	RM	RM	RM
% Failure	100	100	100	100	100	100	100	100
Steel								
Adhesion force, lbf/in. width	--	37.3	--	14.2	96.7	--	42.3	--
Failure Type	RM	RM	RM	RM	RM	RM	RM	RM
% Failure	100	100	100	100	50	100	100	100

R = rubber failure, RC = rubber-cement, CP = cement-primer failure, M = primer-metal failure, RM = rubber metal failure

Chlorinated Polyethylene Rubber to Polyester Cord

More specifically, RX-13845 was evaluated for cord or fabric to rubber adhesion. RX-13845 is an adhesion promoter system consisting of 36 wt.% RX-13804, 36 wt.% Cyrez CRA-138 Resin (a liquid at room temperature), and 28% substrate (synthetic calcium silicate). RX-13845 was prepared by adding preheated Cyrez CRA 138 resin liquid to a dry carrier (substrate) contained in a mixing bowl, followed by addition of preheated RX-13804. The materials were mixed at low speed for 3 minutes. The materials were blended for an additional 3 minutes. RX-13845 permits liquids to be handled as powders. Because the active adhesion promoter is released, the active ingredient is released from the carrier, incorporation of RX-13845 into a rubber compound allows the adhesion promoter to function in the same manner as if it had been incorporated into rubber as a neat material.

The results demonstrate a significant improvement in adhesion of untreated nylon fibers, isocyanate treated nylons, isocyanate treated aramid fibers, and untreated polyester fibers to chlorinated polyethylene polymer. The data is set forth in Table XI, Examples 34-38.

TABLE XI

	Example 35	Example 36	Example 37	Example 38
Tyrin CPE CM 0730	100.00			
N 774 Carbon Black	55.00			
N 650 Carbon Black	30.00			
Albacar 5970(CaCO ₃)	10.00			
PARAPLEX® G-62	15.00			
PLASTHALL® TOTM	30.00			
Calcium Oxide	4.40			
Flectol TMQ	0.20			
RX-13845	---	3.00	6.00	10.00
Subtotal	244.60	247.60	250.60	254.60
Mill Addition				
Vulcup 40KE	9.50			
Triganox 17/40	3.50			
PLB 5405(75%)	6.70			
Total	264.30	267.30	270.30	274.30
Major Variable	Control	RX-13845 (3)	RX-13845 (6)	RX-13845 (10)

Viscosity and Curing Properties

Mooney Viscosity at 132°C(270°F)				
Minimum Viscosity	40.7	40.4	38.2	37.0
t5, minutes	2.2	2.2	2.3	2.3
t10, minutes	2.5	2.5	2.5	2.5
t35, minutes	3.0	3.0	3.2	3.0

TABLE XI (CONT.)

	Example 35	Example 36	Example 37	Example 38
Oscillating Disc Rheometer at 160°C(320°F)				
M _L	9.4	11.9	10	9.4
M _H	48.7	42.2	38.4	37
t _{s2} , minutes	1.3	1.2	1.7	1.5
t' _c (90), minutes	25.8	28.3	29.7	21.8
1.25*t' _c (90), minutes	32.3	35.4	37.1	27.3
Cure Rate Index	4.1	3.7	3.6	4.9
Original Physical Properties				
Stress @ 100% Elongation, MPa	6.4	6.2	6.3	5.4
psi	930	905	920	790
Stress @ 200% Elongation, MPa	11.7	10.9	11.1	9.2
Stress @ 300% Elongation, MPa	---	---	---	---
Tensile Ultimate, MPa	13.5	12.5	12.8	10.5
psi	1965	1820	1850	1530
Elongation @ Break, %	250	255	250	275
Hardness Duro A, pts.	80	80	80	78
Specific Gravity	1.323	1.326	1.324	1.324
UNTREATED NYLON				
Average Adhesion Force, lbf/in width	8.43	7.97	9.63	10.13
std.dev	1.31	1.60	1.23	1.19
ISOCYANATE TREATED NYLON				
Average Adhesion Force, lbf/in width	24.84	27.90	30.24	34.93
std.dev	1.51	4.56	4.54	3.95
Rubber Failure →				
UNTREATED ARAMID				
Average Adhesion Force, lbf/in width	5.54	4.09	6.44	4.80
std.dev	0.57	1.12	0.76	0.46
ISOCYANATE TREATED ARAMID				
Average Adhesion Force, lbf/in width	5.50	8.20	9.78	9.32
std.dev	0.31	1.03	2.27	0.88
UNTREATED POLYESTER				
Average Adhesion Force, lbf/in width	8.90	9.72	17.77	17.39
std.dev	1.33	0.33	4.59	6.49

Method of Measuring Cord Adhesion

Esters were evaluated to determine their effect on adhesion of cords to rubbers when combined with an adhesive resin. The following method is for determining the relative strip-peel adhesion of reinforcing fibers, including natural and manmade filaments and spun yarns, to various rubber compounds and elastomers. This method is conventionally used with industrial weight fibers of 500 denier or greater. Typically, the most common elastomers and compounds employed are natural rubber, styrene butadiene rubber, copolymers of olefins

with non-conjugated dienes (EPDM), polychloroprene rubber (CR), acrylonitrile butadiene elastomer (NBR), chlorosuphonated polyethylene elastomer (CSM), polyisoprene rubber, isobutylene-isoprene copolymeric rubber, chlorinated isobutylene-isoprene copolymeric rubber, brominated isobutylene-isoprene copolymeric rubber, polyvinylchloride, urethane, and blends thereof, but this technique can be modified to determine fiber adhesion to a wide variety of materials.

The adhesion testing described herein was performed in accordance with ASTM D 4393-85 "Strap Peel Adhesion of Reinforcing Cords or Fabrics to Rubber Compounds."

Typically, 1"x 5" strips of fiber/rubber composite materials were prepared for testing. Fibers were positioned onto a tape backing using a rotatable cylinder. The tape backing was applied to a milled elastomer or rubber compound under high temperature and pressure in a hydraulic press (*i.e.*, at curing, extruding, or other conditions) to form a cord- or fabric-reinforced composite material. The composite was then cut into strips for adhesion measurements (*e.g.*, through separation load values, appearance, etc.).

PROCEDURE

An ASTM 429 mold was placed in a compression press (capable of achieving temperatures between 250°F and about 400°F, and a pressure of about 125 tons) and the temperature was set within $\pm 2^\circ\text{F}$ of the vulcanization temperature (cure temperature) for the specific rubber compound used. The press was maintained within the specified temperature range for about 30 minutes.

Three strips of 3" wide masking tape (a suitable masking tape is #515 Masking Tape, Anchor Continental, Inc. Columbia, SC), with adhesive side out, were wrapped around the rotatable cylinder. The three strips were overlapped to achieve a tape backing having a total width of about 7". Six 1" wide fiber samples were wrapped onto the tape backing. The same or different yarn samples can be wound onto each tape backing. Each fiber or cord sample should be wound, however, such that there is no overlapping of fibers and no space between adjacent fibers. Typically, three strips of each fiber sample were prepared and tested.

The fibers were secured with 1" wide masking tape, and the strips were marked A, B, C, D, E, and F. The six wound samples were removed from the cylinder by cutting across the cylinder.

A 5" X 7" piece of unvulcanized compounded rubber to be tested, which has been milled to a specified thickness (0.250 ± 0.20 inches), was cut. The mold surface which will be in contact with the fiber assembly was cleaned with n-heptane.

The preheated mold was removed from the press. The fiber samples were placed at the bottom mold plate with the masking tape backing face down, and the fibers facing up. A 1" X 7" strip of aluminum foil was placed on the back edge of the fiber samples so that the fibers are perpendicular to the aluminum foil and about one inch of their length covers the aluminum foil strip. Each strip has a specified position in the press. The cleaned 5" X 7" unvulcanized rubber slab was then on top on the fiber assembly. The preheated top mold plate was placed on top of the samples to form a sandwich of mold top plate, rubber compound, aluminum foil, yarn samples, tape and bottom plate. This sandwich is then placed in the preheated compression press and a pressure of about 125 tons is applied. The pressure and temperature are maintained for the specified time (cure time).

The mold assembly was removed from the press at the end of the cure time. It is important not to disturb the fiber composite while separating the pad from the mold plates. Typically, the pad was placed in cold water to expedite the cooling process. The pad was cooled to ambient temperature prior to marking the pad for identification.

The adhesion pad should sit for an extended period ("conditioning period"), e.g., overnight, prior to cutting into the 1" x 5" strips for adhesion testing. As much of the aluminum foil strip as possible was removed to give a starting separation between the fiber sample and the rubber compound. The foil can be left in place if too difficult to remove. After conditioning, each 5" x 7" rubber section was cut into six 1" x 5" strips such that only one fiber to be tested is contained in each strip.

Each 1" x 5" adhesion composite strip was tested on the Instron 4201 tensile/compression machine (Instron Corporation, Canton, MA) according to method 08 of the Instron Series IX Materials Testing™ Software.

TABLE XII

Material	Chemical Description	Supplier
SMR-L	Natural rubber	Alcan
Kadox 930	Zinc Oxide	The C.P. Hall Company
Stearic Acid R.G.	Stearic Acid, rubber grade	The C.P. Hall Company
N-330	Carbon Black	JM Huber or Degussa
Spider Sulfur	Elemental Sulfur	The C.P. Hall Company
Santocure TBSI	N-tert-butyl-di(2-benzothiazolesulfen)imide	Harwick Standard
RX-13577	Tridecyl tallate	The C.P. Hall Company
RX-13804	Di(2-ethylhexyl)dimerate	The C.P. Hall Company
RX-13824	Ditridecyl Dimerate	The C.P. Hall Company
Plasthall DOS	Diocetyl sebacate	The C.P. Hall Company
Paraplex A-8000	Polyester Adipate	The C.P. Hall Company
Staflex DBM	Dibutyl maleate	The C.P. Hall Company
DiCup 40 KE	Dicumyl Peroxide on Burgess Clay	Hercules
RX-13845	36% RX-13804, 36% Cyrez® D-148M, 28% Hydrated Amorphous Silica	The C.P. Hall Company
Cyrez® Resin D-148M	Melamine Resin Powder Concentrate	Cytec
N-326	Carbon Black	JM Huber
Cobalt Naphthenate	Metal Carboxylate adhesion promoter	Sheperd
Santoflex 13	N-Isopropyl-N'-phenyl-p-phenylenediamine	Harwick
PVI	N-(cyclohexylthio) phthalimide	Flexsys
Pennacolite Resin	Formaldehyde Resin	Indspec
Vulkacit DZ	Benzothiazyl-2-dicyclohexyl-sulfenamide	Bayer
Resimene	Hexamethoxymelamine	Solutia
Nordel IP3720	Hydrocarbon Rubber	DuPont
N762	Carbon Black	JM Huber
Ricon 150	Liquid Polybutadiene	Ricon
TMTD	Tetramethyl thiuram disulfide	R.T. Vanderbilt
Rotax	2-mercaptobenzothiazole	R.T. Vanderbilt
SR 350	Acrylic Ester	Sartomer
UBS020602	Di(2-ethylhexyl) dimerate, hydrogenated	The C.P. Hall Company
Cyrez® Resin CRA-133M	Melamine Resin Powder concentrate	Cytec
Cyrez® Resin CRA-148M	Melamine Resin Powder concentrate	Cytec
Royalene 501	Ethylene-propylene ethylidene norbornene rubber 57/43 EP Ratio	Uniroyal
Royalene 502	ENB third monomer 62/38 EP ratio	Uniroyal
N-550	Carbon Black	Engineering Carbon
RX-13782	Capric Tallate	The C. P. Hall Company

TABLE XII (CONT.)

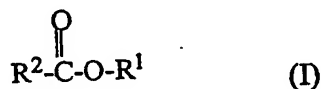
Material	Chemical Description	Supplier
RX-13805	Di(2-ethylhexyl) dimerate	The C. P. Hall Company
RX-13806	Didecyl dimerate	The C. P. Hall Company
RX-13853	Di-hexyldecyl tallate	The C. P. Hall Company
UBS 020602	Di (2-ethylhexyl) dimerate (Pripol 1006)	The C. P. Hall Company
UBS 120601	polyester dimerate	The C. P. Hall Company
UBS 121201	polyester dimerate	The C. P. Hall Company
Sunpar 2280	Paraffinic Oil	Sun Oil
Premix MBT	2-mercaptobenzothiazole	The C. P. Hall Company
Premix TMTD	Tetramethyl thiuram disulfide	The C. P. Hall Company
Premix DPTT	Dipentamethylene thiurum (tetra)sulfide	The C. P. Hall Company
Premix TDEC	Tellurium diethyldithiocarbamate	The C. P. Hall Company
UBS051602	Dioleyl dimerate	The C. P. Hall Company
UBS060302	Ditridecyl dimerate	The C. P. Hall Company
BM050702	Pentaerythritol tetratallate	The C. P. Hall Company
Royalene IM7200	blend of ethylene-propylene-ethylidene norbornene rubber with polyethylene dust 76/24 EP Ratio	Uniroyal
RX-13822	Tridecyl dimerate	The C. P. Hall Company
RX-13823	Polyester dimerate	The C. P. Hall Company
Trigonox 145-45B-pd	2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3, 45% supported on calcium carbonate	Akzo Nobel
Tyrin CPE CM 0730	chlorinated polyethylene 30% chlorine	Dupont Dow
N-774	carbon black	Degussa Engineered Carbons
N-650	carbon black	Degussa Engineered Carbons
Albacar 5970	calcium carbonate	The C. P. Hall Company
Paraplex G-62	epoxidized soybean oil	The C. P. Hall Company
RX-13845	Micro Cel E 28 wt.%, RX-13804 36 wt.%, Cyrez® CRA-138M 36 wt.%	The C. P. Hall Company
Micro Cel E	Calcium Silicate	The C. P. Hall Company
Cyrez® CRA-138M	Melamine Formaldehyde resin	Cytec
Cyrez® CRA-148M	Melamine Formaldehyde resin	Cytec
VulCup 40KE	2,2'-bis(tert-butylperoxy) diisopropylbenzene	Harwick Standard
Triganox 17/40	4,4-bis(tert-butyl peroxy) - 3,3,5-trimethylcyclohexane	Akzo Nobel
PLB 5405 (75%)	Trimethylolpropane trimethyl acrylate	Flow Polymer Incorporated
SMR CV 60	Natural Rubber	
Process Oil C-255E	Paraffinic Oil	The C. P. Hall Company
RX-13896	Di(2-ethylhexyl) dimerate	The C. P. Hall Company

TABLE XII (CONT.)

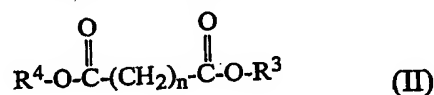
Material	Chemical Description	Supplier
	(Unidyme 22)	
Sulfur	Sulfur	The C. P. Hall Company
Santocure TBBS	N-t-butyl-2-benzothiazolesulfenamide	Harwick Standard
Hallco TE-577	Tridecyl Tallate	The C. P. Hall Company
RX-13653	pentaerythritol tetratallate	The C. P. Hall Company
RX-13892	Diolcyl dimerate	The C. P. Hall Company
Calcium Oxide	Calcium Oxide	The C. P. Hall Company
Plasthall TOTM	72 wt.% Trioctyl Trimellitate, 28 wt.% Hydrated Amorphous Silica	The C. P. Hall Company
Flectol TMQ	2,2,4-Trimethyl-1,2-dihydroquinoline, polymerized	Flexsys
	Untreated nylon fiber	Beaver Manufacturing Co.
Powerloc	Isocyanate treated nylon fiber	Beaver Manufacturing Co.
	Untreated aramid fiber	Beaver Manufacturing Co.
Beaverloc	Isocyanate treated aramid fiber	Beaver Manufacturing Co.
	Untreated polyester fiber	Beaver Manufacturing Co.

WHAT IS CLAIMED IS:

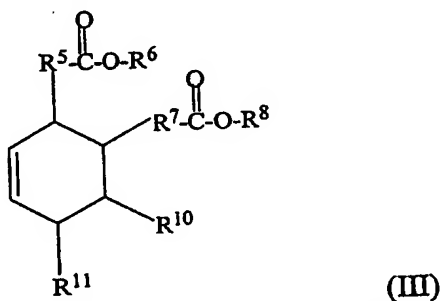
1. A rubber composition comprising rubber selected from the group consisting of natural rubber, synthetic rubber, and a combination thereof; and an adhesion promoter containing (1) an adhesive resin in an amount of about 0.1% to about 15% by weight, based on the weight of rubber in the composition; and (2) an ester having formula I, II, III, IV or a combination of any two or more of said esters in an amount of about 0.1% to about 15% by weight, based on the weight of rubber in the composition:



wherein R^1 is a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; R^2 is a C_3 - C_{24} saturated fatty acid residue, or an unsaturated fatty acid residue having 1 to 6 carbon-to-carbon double bonds;



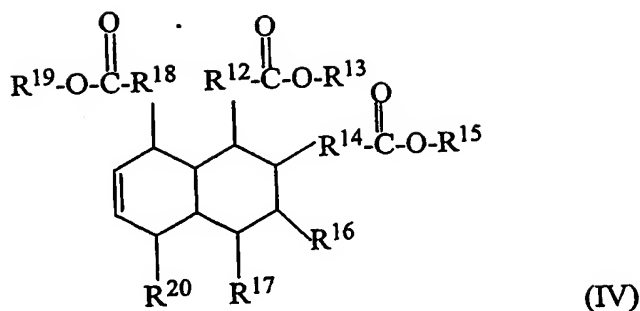
wherein $n=3-24$, and R^3 and R^4 , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds;



wherein R^5 and R^7 , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{10} and R^{11} , same or different, are a C_3 - C_{24} , saturated hydrocarbon chain, straight chain or branched; or an unsaturated C_3 - C_{24} , hydrocarbon chain, straight chain or branched, having 1 to 6, carbon-to-carbon double bonds;

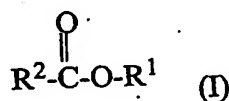


wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} , hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

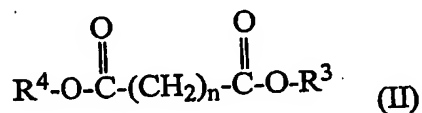
R^{13} , R^{15} and R^{19} , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

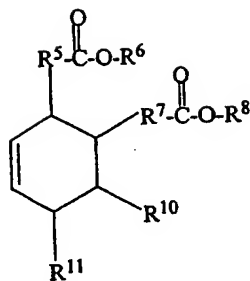
2. A rubber composition in accordance with claim 1, wherein the ester is selected from the group consisting of formula I, II, III, IV, and a combination of any two or more of said esters:



wherein R^1 is a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and R^2 is a C_8 - C_{18} saturated fatty acid residue, or an unsaturated fatty acid residue having 1 to 3 carbon-to-carbon double bonds;



wherein $n=6-18$, and R^3 and R^4 , same or different, are a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds;

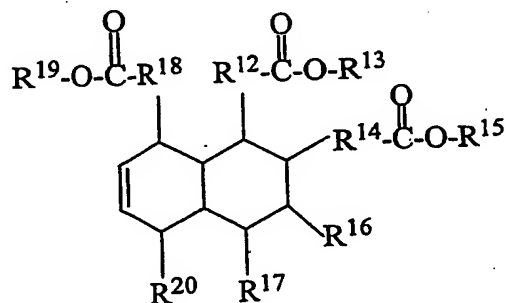


(III)

wherein R^5 and R^7 , are a C_6 - C_{24} hydrocarbon chain, straight chain or branched; either saturated or having 1 to 3 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{10} and R^{11} , same or different, are a C_3 - C_{18} , saturated hydrocarbon chain, straight chain or branched; or an unsaturated hydrocarbon chain, straight chain or branched, containing 1 to 3 carbon-to-carbon double bonds;



(IV)

wherein R^{12} , R^{14} and R^{18} , same or different, are a C_8 - C_{18} , hydrocarbon chain, straight chain or branched, either saturated or having 1 to 3 carbon-to-carbon double bonds;

R^{13} , R^{15} and R^{19} , same or different, are a C_6 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_6 - C_{18} saturated hydrocarbon chain, straight chain or branched; or an unsaturated C_6 - C_{18} hydrocarbon chain, straight chain or branched, containing 1 to 3 carbon-to-carbon double bonds.

3. The rubber composition of claim 1, wherein the adhesive resin is a condensation product of a methylene acceptor and a methylene donor.

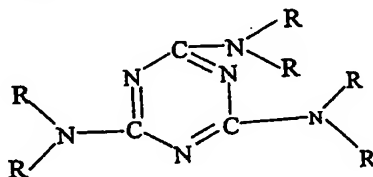
4. The rubber composition in accordance with claim 3, wherein the adhesive resin is selected from the group consisting of phenol-formaldehyde, melamine-formaldehyde; naphthol-formaldehyde; polyepoxide; a reaction product of triallyl cyanurate, resorcinol, and formaldehyde; a reaction product of p-chlorophenol, resorcinol, and formaldehyde; a copolymer of styrene, butadiene, and 2-vinylpyridine; and mixtures thereof.

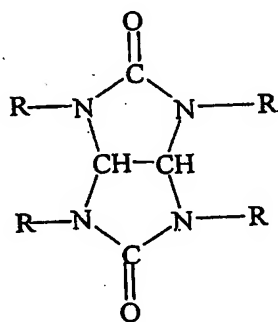
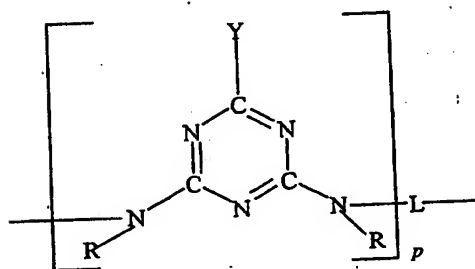
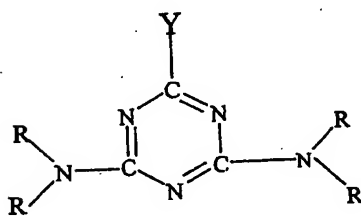
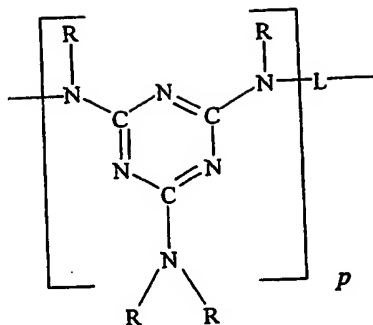
5. The rubber composition in accordance with claim 4, wherein the phenol-formaldehyde resin is resorcinol-formaldehyde.

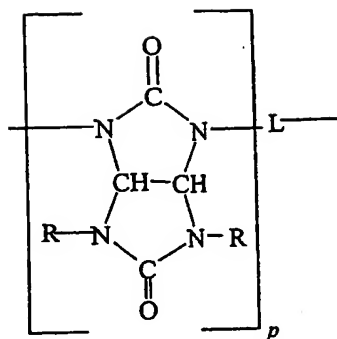
6. The rubber composition in accordance with claim 1, wherein the adhesive resin is selected from the group consisting of derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril monomers and oligomers of these monomers, which have been substituted on average at two or more positions on the monomer or on each unit of the oligomer with vinyl terminated radicals, the vulcanizable rubber composition being free of resorcinol.

7. The vulcanizable rubber composition in accordance with claim 6, wherein at least one of the adhesive resins has been further substituted on average at one or more positions with a radical which comprises carbamoylmethyl or amidomethyl.

8. A vulcanizable rubber composition in accordance with claim 6, wherein the adhesive resin is selected from compounds of the formula:

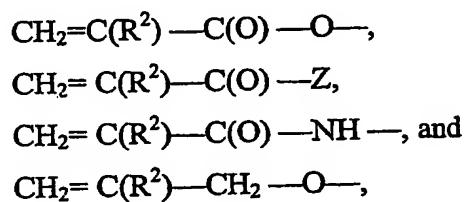




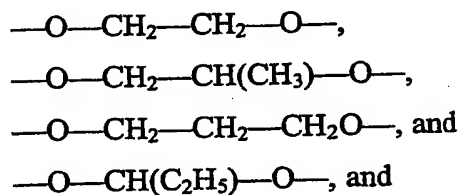


and positional isomers thereof,

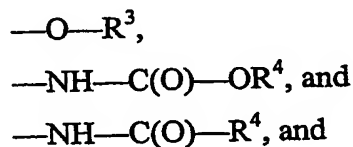
wherein, in each monomer and in each polymerized unit of the oligomers, Y is selected from methyl, phenyl and cyclohexyl, and, on average, at least two R are $-\text{CH}_2\text{-R}^1$, and any remaining R are H, and at least 2 R^1 are radicals selected from



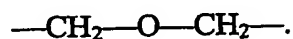
wherein R^2 is hydrogen or $\text{C}_1\text{-C}_{18}$ alkyl, and Z is a radical selected from



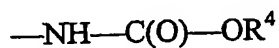
any remaining R^1 radicals are selected from



wherein R_3 is hydrogen or R_4 , and R_4 is a $\text{C}_1\text{-C}_{18}$ alkyl, alicyclic, hydroxyalkyl, alkoxyalkyl or aromatic radical, and in the oligomers, P is 2 to about 10, and L is methylene or the radical

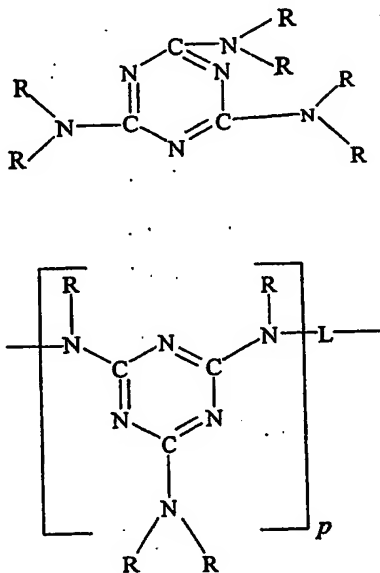


9. A vulcanizable rubber composition in accordance with claim 8, wherein on average at least one R^1 in each monomer or in each oligomerized unit of the adhesive resin is:



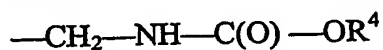
wherein R^4 is as defined in claim 8.

10. A vulcanizable rubber composition in accordance with claim 9, wherein the adhesive resin is a compound of the formula



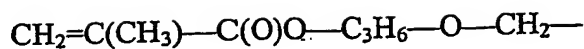
wherein P, L and R are as defined in claim 8.

11. A vulcanizable rubber composition in accordance with claim 10, wherein in the adhesive resin formulas, on average at least one R radical in each monomer or in each oligomerized unit is

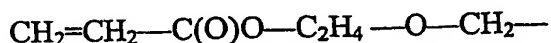


wherein R^4 is a $\text{C}_1\text{-C}_{18}$ alkyl, alicyclic, hydroxyalkyl, alkoxyalkyl or aromatic radical.

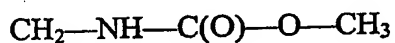
12. A vulcanizable rubber composition in accordance with claim 10, wherein on average at least two R radicals are selected from



and



and at least one R radical is selected from



and



13. A vulcanizable rubber composition in accordance with claim 8, further comprising an additional additive selected from hydroxymethylated and alkoxymethylated (alkoxy having 1-5 carbon atoms) derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril and their oligomers.

14. The composition in accordance with claim 6, wherein the adhesive resin is a derivative of melamine or an oligomer of melamine.

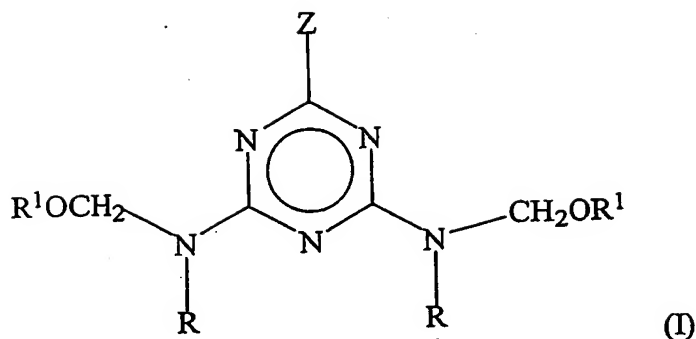
15. The composition in accordance with claim 6, wherein the adhesive resin is a derivative of acetoguanamine or an oligomer of acetoguanamine.

16. The composition in accordance with claim 6, wherein the adhesive resin is a derivative of benzoguanamine or an oligomer of benzoguanamine.

17. The composition in accordance with claim 6, wherein the adhesive resin is a derivative of cyclohexylguanamine or an oligomer of cyclohexylguanamine.

18. A vulcanizable rubber composition in accordance with claim 1, wherein the adhesive resin is a self-condensing alkylated triazine resin selected from the group consisting of (i), (ii), and (iii):

(i) a self-condensing alkylated triazine resin having at least one of imino or methylol functionality and represented by formula (I)



(ii) an oligomer of (i), or

(iii) a mixture of (i) and (ii), wherein

Z is -N(R)(CH₂OR¹), aryl having 6 to 10 carbon atoms, alkyl having 1 to 20 carbon atoms or an acetyl group,

each R is independently hydrogen or -CH₂OR¹, and

each R¹ is independently hydrogen or an alkyl group having 1 to 12 carbon atoms,

provided that at least one R is hydrogen or -CH₂OH and at least one R¹ is selected from the alkyl group; and

wherein the vulcanizable rubber composition is substantially free of methylene acceptor coreactants.

19. The vulcanizable rubber composition in accordance with claim 18, wherein at least one R group is hydrogen.

20. The vulcanizable rubber composition in accordance with claim 19, wherein at least one R¹ group is a lower alkyl group having 1 to 6 carbon atoms.

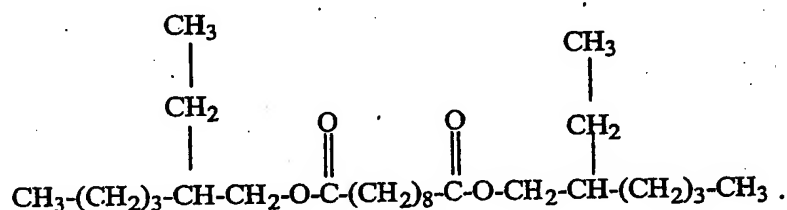
21. The vulcanizable rubber composition in accordance with claim 20, wherein the adhesive resin is a derivative of melamine, benzoguanamine, cyclohexylguanamine, or acetoguanamine, or an oligomer thereof.

22. The vulcanizable rubber composition in accordance with claim 20, wherein Z is -N(R)(CH₂OR¹).

23. The rubber composition in accordance with claim 4, wherein the phenol-formaldehyde resin is resorcinol-formaldehyde; and the melamine-formaldehyde resin is N-(substituted oxymethyl) melamine-formaldehyde.

24. A rubber composition in accordance with claim 1, wherein the ester has the formula II and comprises a saturated diester formed by the reaction of sebacic acid and a C₆-C₂₄ alcohol, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

25. A rubber composition in accordance with claim 24, wherein the alcohol is 2-ethylhexyl alcohol, and the ester has the following formula:



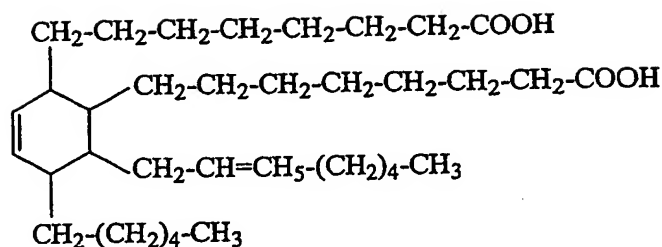
26. A rubber composition in accordance with claim 1, wherein the ester is an unsaturated diester formed by the reaction of a C₃₆ dimer acid and a C₃-C₁₈ alcohol, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

27. A rubber composition in accordance with claim 26, wherein the alcohol is 2-ethylhexyl alcohol.

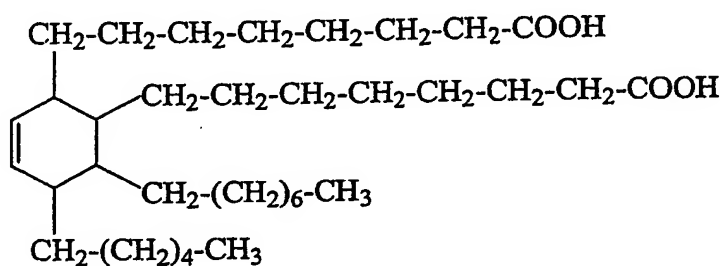
28. A rubber composition in accordance with claim 26, wherein the alcohol is tridecyl alcohol.

29. A rubber composition in accordance with claim 26, wherein the alcohol is oleyl alcohol.

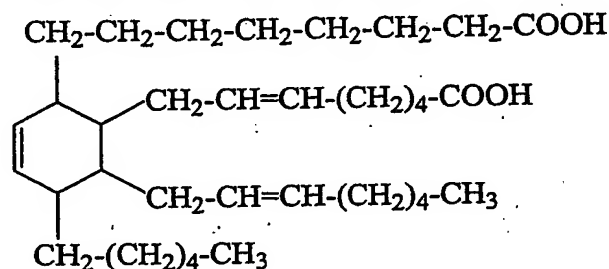
30. A rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



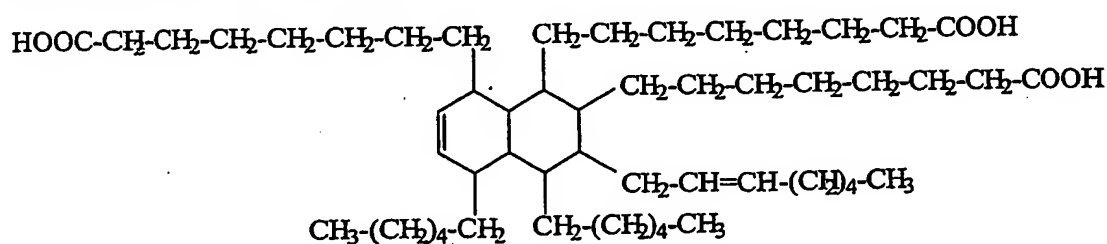
31. A rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



32. A rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



33. A rubber composition in accordance with claim 1, wherein the ester is the reaction product of a C₃-C₂₄ alcohol with a tricarboxylic acid, having the following formula:



34. A rubber composition in accordance with claim 1, wherein the ester is a combination of compounds of formula I, II, III, and IV.

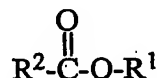
35. A rubber composition in accordance with claim 34, wherein the ester is a reaction product of a C₃-C₂₄ alcohol straight chain or branched, saturated or unsaturated having 1 to 3 carbon-to-carbon double bonds, with a dimer acid having CAS #61788-89-4.

36. A rubber composition in accordance with claim 35, wherein the alcohol is 2-ethylhexyl alcohol.

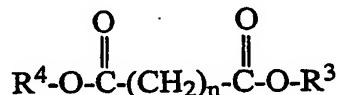
37. A rubber composition in accordance with claim 35, wherein the alcohol is a tridecyl alcohol.

38. A rubber composition in accordance with claim 35, wherein the alcohol is an oleyl alcohol.

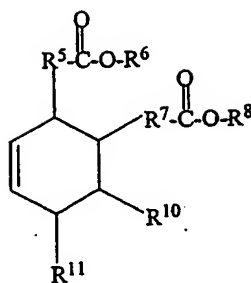
39. A method of increasing the adhesion of a rubber composition to a polymer, glass, or metal substrate, said rubber composition including a natural or synthetic rubber, a rubber vulcanizing agent, and an adhesive resin, comprising adding to said rubber composition, in an amount of about 0.1% to 15% by weight, based on the weight of the rubber, an ester having formula I, II, III, IV, or mixtures thereof:



wherein R¹ is a C₃-C₂₄ alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; R² is a C₃-C₂₄ saturated fatty acid residue, or an unsaturated fatty acid residue having 1 to 6 carbon-to-carbon double bonds;



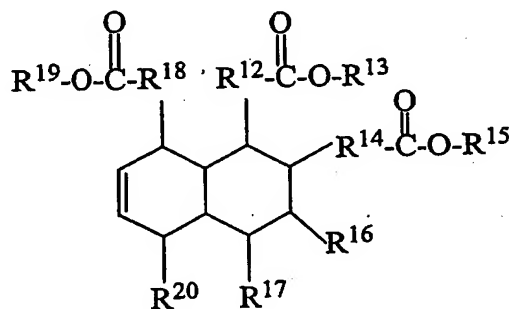
wherein n=3-24 and R³ and R⁴, same or different, are a C₃-C₂₄ alkyl radical, straight chain or branched;



wherein R^5 and R^7 , same or different, are a C_3 - C_{24} hydro carbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched; and

R^{10} and R^{11} , same or different, are a C_3 - C_{24} , saturated hydrocarbon chain, straight chain or branched; or an unsaturated C_3 - C_{24} , hydrocarbon chain, straight chain or branched, having 1 to 6 carbon-to-carbon double bonds;



wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^{13} , R^{15} and R^{19} , same or different, are C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

40. A method in accordance with claim 39, wherein the substrate is a plurality of cords.

41. A method in accordance with claim 39, wherein the substrate is a polymeric sheet or fabric.

42. A method in accordance with claim 39, wherein the substrate is metal flat stock material.

43. A cord-reinforced article of manufacture comprising a plurality of cords selected from polymeric cords, metal cords, glass cords, and a combination thereof, adhered to the rubber composition of claim 1.

44. The rubber composition in accordance with claim 1, wherein the R^2 , R^5 , R^7 , R^{12} , R^{14} are fatty acid residues derived from animal or vegetable fatty acids.

45. The rubber composition of claim 44, wherein the fatty acids are selected from the group consisting of butter; lard; tallow; grease; herring; menhaden; pilchard; sardine; babassu; castor; coconut; corn; cottonseed; jojoba; linseed; oiticia; olive; palm; palm kernel; peanut; rapeseed; safflower; soya; sunflower; tall; tung; and mixtures thereof.

46. The rubber composition of claim 45, wherein the fatty acid residues are selected from the group consisting of hexanoic; octanoic; decanoic; dodecanoic; 9-dodecenoic; tetradecanoic; 9-tetradecenoic; hexadecanoic; 9-hexadecenoic; octadecanoic; 9-octadecenoic; 9-octadecenoic, 12-hydroxy; 9, 12-octadecadienoic; 9, 12, 15-octadecatrienoic; 9, 11, 13-octadecatrienoic; 9, 11, 13-octadecatrienoic, 4-oxo; octadecatetrenoic; eicosanoic; 11-eicosenoic; eicosadienoic; eicosatrienoic; 5, 8, 11, 14-eicosatetraenoic; eicosapentaenoic; docosanoic; 13-docosenoic; docosatetraenoic; 4, 8, 12, 15, 19-docosapentaenoic; docosahexaenoic; tetracosenoic; and 4, 8, 12, 15, 18, 21-tetracosahexaenoic.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/14411

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L21/00 C08K5/10 C08K5/3492

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/010275 A1 (FANTOZZI JUSTIN JOSEPH ET AL) 24 January 2002 (2002-01-24) page 1, paragraph 5 - paragraph 12 page 1, paragraph 17 page 3, paragraph 35 example 1; tables 1,2 claims 1-4	1, 3-5, 23-25, 44-46
Y	EP 1 022 306 A (KF INTERNATIONAL CO LTD ;BRIDGESTONE CORP (JP)) 26 July 2000 (2000-07-26) page 3, line 14 - line 53 page 4, line 1 - line 2 page 4, line 25 - line 29 page 6, line 42 - line 49 example 16; table 2 claims 1-3	1-5, 39-41, 43-46

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the international search

4 September 2003

Date of mailing of the international search report

15/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Denis, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/14411

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>US 4 550 147 A (OOHARA RIICHIRO) 29 October 1985 (1985-10-29)</p> <p>column 1, line 51 -column 2, line 66 column 3, line 10 - line 16 tables 1,2 claims 1,2</p> <p>-----</p>	<p>1-5, 39-41, 43-46</p>

INTERNATIONAL SEARCH REPORT

In addition on patent family members

International Application No

PCT/US 03/14411

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2002010275	A1	24-01-2002	US 6405775 B1	18-06-2002
			BR 0102148 A	01-10-2002
			DE 10127616 A1	01-08-2002
			GB 2363124 A	12-12-2001
			JP 2002234310 A	20-08-2002
EP 1022306	A	26-07-2000	JP 2000212335 A	02-08-2000
			EP 1022306 A1	26-07-2000
			US 6525121 B1	25-02-2003
US 4550147	A	29-10-1985	NONE	

CORRECTED VERSION

(19) World Intellectual Property
Organization
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(71) Applicant: THE C.P. HALL COMPANY [US/US]; 311
South Wacker Drive, Suite 4700, Chicago, IL 60606-6622
(US).

(72) Inventors: WENTWORTH, Gary; 5540 North Wayne
Avenue, Chicago, IL 60640 (US). O'ROURKE, Stephen;
1847 Marne Road, Bolingbrook, IL 60490 (US). STE-
FANISIN, Kimberly; 4867 Wick Drive, Oak Lawn, IL
60453 (US). ENGLISH, John; 11000 S. Keeler, Oak
Lawn, IL 60453 (US).

(74) Agent: ANDERSON, Richard, H.; Marshall, Gerstein
& Borun, 6300 Sears Tower, 233 South Wacker Drive,
Chicago, IL 60606 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
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GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD,
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VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
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Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
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SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
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see PCT Gazette No. 01/2004 of 31 December 2003, Sec-
tion II

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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: ADHESION PROMOTER FOR CORD-REINFORCED RUBBER AND METAL OR POLYMER SUBSTRATE/RUB-
BER COMPOSITES

(57) Abstract: A rubber composition including a natural or synthetic rubber, and an adhesive resin capable of unexpected adhesion
to metal, polymer and glass substrates, particularly cords in radical tires, hoses, conveyor belts, transmission belts, and the like by
the addition of long chain esters, including mono-, di- and tri-esters.

WO 2003/095550 A1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
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(26) Publication Language: English

(30) Priority Data:
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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

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(71) Applicant: THE C.P. HALL COMPANY [US/US]; 311 South Wacker Drive, Suite 4700, Chicago, IL 60606-6622 (US).

(72) Inventors: WENTWORTH, Gary; 5540 North Wayne Avenue, Chicago, IL 60640 (US). O'ROURKE, Stephen; 1847 Marne Road, Bolingbrook, IL 60490 (US). STEFANISIN, Kimberly; 4867 Wick Drive, Oak Lawn, IL 60453 (US). ENGLISH, John; 11000 S. Keeler, Oak Lawn, IL 60453 (US).

(74) Agent: ANDERSON, Richard, H.; Marshall, Gerstein & Borun, 6300 Sears Tower, 233 South Wacker Drive, Chicago, IL 60606 (US).

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Previous Correction:

see PCT Gazette No. 01/2004 of 31 December 2003, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

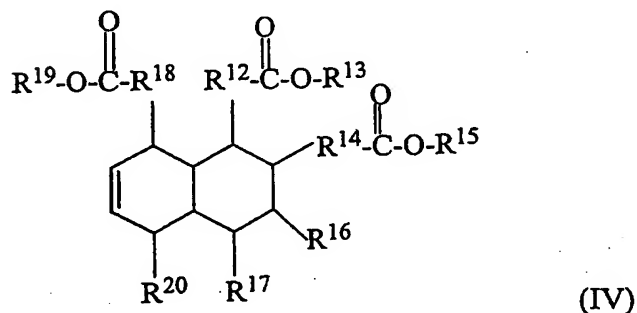
(54) Title: ADHESION PROMOTER FOR CORD-REINFORCED RUBBER AND METAL OR POLYMER SUBSTRATE/RUBBER COMPOSITES

(57) Abstract: A rubber composition including a natural or synthetic rubber, and an adhesive resin capable of unexpected adhesion to metal, polymer and glass substrates, particularly cords in radical tires, hoses, conveyor belts, transmission belts, and the like by the addition of long chain esters, including mono, di- and tri-esters.

WO 2003/095550 A1

AMENDED CLAIMS

Received by the International Bureau on 17 November 2003 :
 Claims 2,3,6-22,24-38,40-42,45-46 amended, 47-49 added.

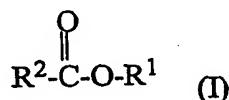


wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} , hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

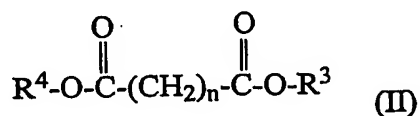
R^{13} , R^{15} and R^{19} , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

2. The rubber composition in accordance with claim 1, wherein the ester is selected from the group consisting of formula I, II, III, IV, and a combination of any two or more of said esters:



wherein R^1 is a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and R^2 is a C_8 - C_{18} saturated fatty acid residue, or an unsaturated fatty acid residue having 1 to 3 carbon-to-carbon double bonds;



wherein $n=6-18$, and R^3 and R^4 , same or different, are a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds;

3. The rubber composition in accordance with claim 1, wherein the adhesive resin is a condensation product of a methylene acceptor and a methylene donor.

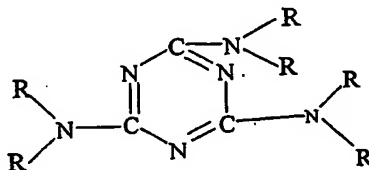
4. The rubber composition in accordance with claim 3, wherein the adhesive resin is selected from the group consisting of phenol-formaldehyde, melamine-formaldehyde; naphthol-formaldehyde; polyepoxide; a reaction product of triallyl cyanurate, resorcinol, and formaldehyde; a reaction product of p-chlorophenol, resorcinol, and formaldehyde; a copolymer of styrene, butadiene, and 2-vinylpyridine; and mixtures thereof.

5. The rubber composition in accordance with claim 4, wherein the phenol-formaldehyde resin is resorcinol-formaldehyde.

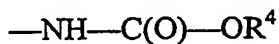
6. The rubber composition in accordance with claim 1, wherein the adhesive resin is selected from the group consisting of derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril monomers and oligomers of these monomers, which have been substituted on average at two or more positions on the monomer or on each unit of the oligomer with vinyl terminated radicals, the rubber composition being free of resorcinol.

7. The rubber composition in accordance with claim 6, wherein at least one of the adhesive resins has been further substituted on average at one or more positions with a radical which comprises carbamoylmethyl or amidomethyl.

8. The rubber composition in accordance with claim 6, wherein the adhesive resin is selected from compounds of the formula:

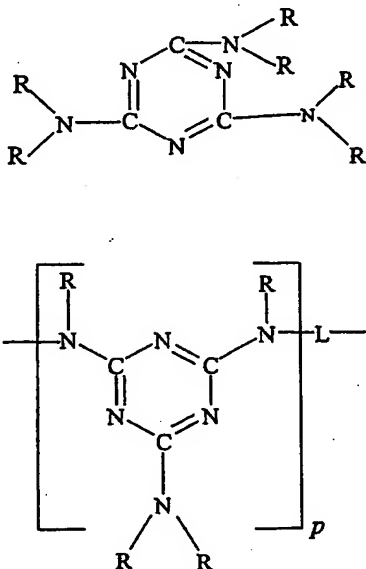


9. The rubber composition in accordance with claim 8, wherein on average at least one R^1 in each monomer or in each oligomerized unit of the adhesive resin is:



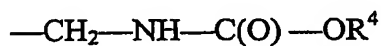
wherein R^4 is as defined in claim 8.

10. The rubber composition in accordance with claim 9, wherein the adhesive resin is a compound of the formula



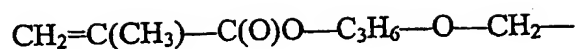
wherein P, L and R are as defined in claim 8.

11. The rubber composition in accordance with claim 10, wherein in the adhesive resin formulas, on average at least one R radical in each monomer or in each oligomerized unit is

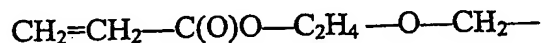


wherein R^4 is a $\text{C}_1\text{-C}_{18}$ alkyl, alicyclic, hydroxyalkyl, alkoxyalkyl or aromatic radical.

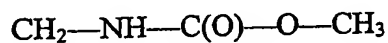
12. The rubber composition in accordance with claim 10, wherein on average at least two R radicals are selected from



and



and at least one R radical is selected from



and



13. The rubber composition in accordance with claim 8, further comprising an additional additive selected from hydroxymethylated and alkoxymethylated (alkoxy having 1-5 carbon atoms) derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril and their oligomers.

14. The rubber composition in accordance with claim 6, wherein the adhesive resin is a derivative of melamine or an oligomer of melamine.

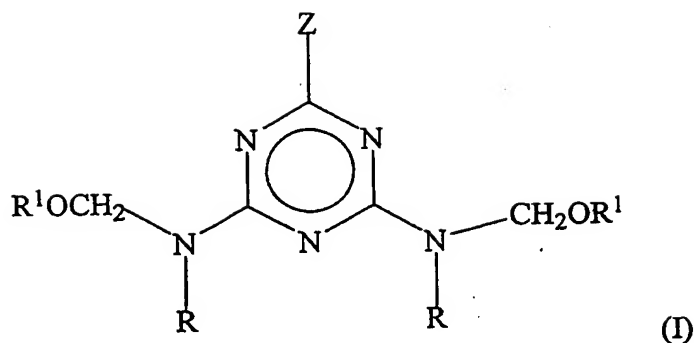
15. The rubber composition in accordance with claim 6, wherein the adhesive resin is a derivative of acetoguanamine or an oligomer of acetoguanamine.

16. The rubber composition in accordance with claim 6, wherein the adhesive resin is a derivative of benzoguanamine or an oligomer of benzoguanamine.

17. The rubber composition in accordance with claim 6, wherein the adhesive resin is a derivative of cyclohexylguanamine or an oligomer of cyclohexylguanamine.

18. The rubber composition in accordance with claim 1, wherein the adhesive resin is a self-condensing alkylated triazine resin selected from the group consisting of (i), (ii), and (iii):

(i) a self-condensing alkylated triazine resin having at least one of imino or methylol functionality and represented by formula (I)



(ii) an oligomer of (i), or

(iii) a mixture of (i) and (ii), wherein

Z is -N(R)(CH₂OR¹), aryl having 6 to 10 carbon atoms, alkyl having 1 to 20 carbon atoms or an acetyl group,

each R is independently hydrogen or -CH₂OR¹, and

each R¹ is independently hydrogen or an alkyl group having 1 to 12 carbon atoms,

provided that at least one R is hydrogen or -CH₂OH and at least one R¹ is selected from the alkyl group; and

wherein the rubber composition is substantially free of methylene acceptor coreactants.

19. The rubber composition in accordance with claim 18, wherein at least one R group is hydrogen.

20. The rubber composition in accordance with claim 19, wherein at least one R¹ group is a lower alkyl group having 1 to 6 carbon atoms.

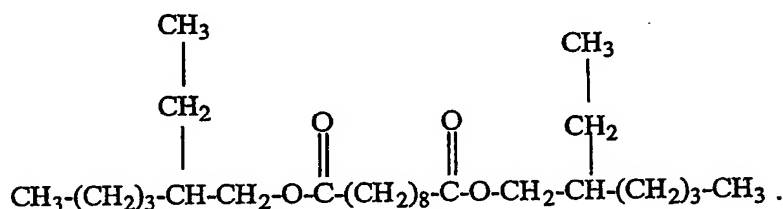
21. The rubber composition in accordance with claim 20, wherein the adhesive resin is a derivative of melamine, benzoguanamine, cyclohexylguanamine, or acetoguanamine, or an oligomer thereof.

22. The rubber composition in accordance with claim 20, wherein Z is -N(R)(CH₂OR¹).

23. The rubber composition in accordance with claim 4, wherein the phenol-formaldehyde resin is resorcinol-formaldehyde; and the melamine-formaldehyde resin is N-(substituted oxymethyl) melamine-formaldehyde.

24. The rubber composition in accordance with claim 1, wherein the ester has the formula II and comprises a saturated diester formed by the reaction of sebacic acid and a C₆-C₂₄ alcohol, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

25. The rubber composition in accordance with claim 24, wherein the alcohol is 2-ethylhexyl alcohol, and the ester has the following formula:



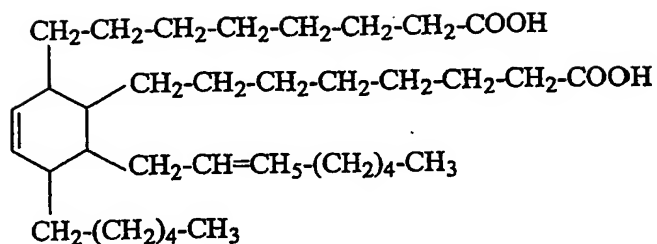
26. The rubber composition in accordance with claim 1, wherein the ester is an unsaturated diester formed by the reaction of a C₃₆ dimer acid and a C₃-C₁₈ alcohol, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

27. The rubber composition in accordance with claim 26, wherein the alcohol is 2-ethylhexyl alcohol.

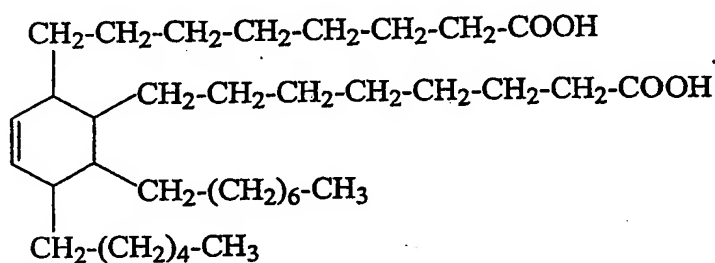
28. The rubber composition in accordance with claim 26, wherein the alcohol is tridecyl alcohol.

29. The rubber composition in accordance with claim 26, wherein the alcohol is oleyl alcohol.

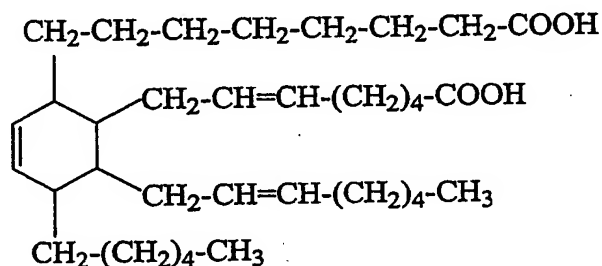
30. The rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



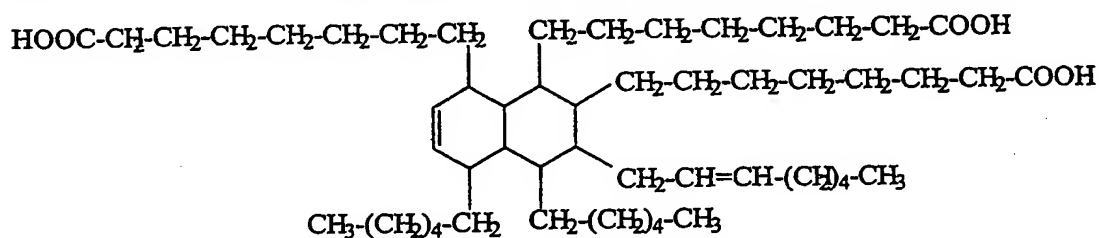
31. The rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



32. The rubber composition in accordance with claim 1, wherein the ester comprises the following dimer acid reacted with a C₃-C₂₄ alcohol:



33. The rubber composition in accordance with claim 1, wherein the ester is the reaction product of a C₃-C₂₄ alcohol with a tricarboxylic acid, having the following formula:



34. The rubber composition in accordance with claim 1, wherein the ester is a combination of compounds having formula I, II, III and IV.

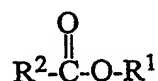
35. The rubber composition in accordance with claim 34, wherein the ester is a reaction product of a C₃-C₂₄ alcohol straight chain or branched, saturated or unsaturated having 1 to 3 carbon-to-carbon double bonds, with a dimer acid having CAS #61788-89-4.

36. The rubber composition in accordance with claim 35, wherein the alcohol is 2-ethylhexyl alcohol.

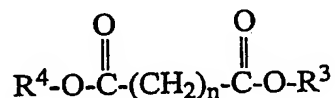
37. The rubber composition in accordance with claim 35, wherein the alcohol is a tridecyl alcohol.

38. The rubber composition in accordance with claim 35, wherein the alcohol is an oleyl alcohol.

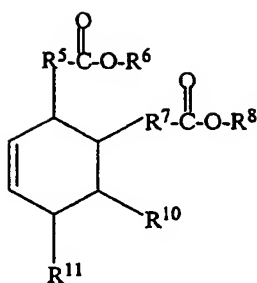
39. A method of increasing the adhesion of a rubber composition to a polymer, glass, or metal substrate, said rubber composition including a natural or synthetic rubber, a rubber vulcanizing agent, and an adhesive resin, comprising adding to said rubber composition, in an amount of about 0.1% to 15% by weight, based on the weight of the rubber, an ester having formula I, II, III, IV, or mixtures thereof:



wherein R¹ is a C₃-C₂₄ alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; R² is a C₃-C₂₄ saturated fatty acid residue, or an unsaturated fatty acid residue having 1 to 6 carbon-to-carbon double bonds;



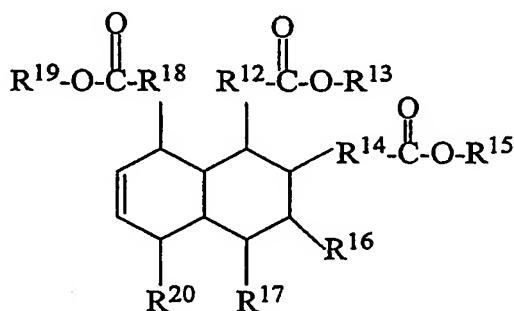
wherein n=3-24 and R³ and R⁴, same or different, are a C₃-C₂₄ alkyl radical, straight chain or branched;



wherein R^5 and R^7 , same or different, are a C_3 - C_{24} hydro carbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched; and

R^{10} and R^{11} , same or different, are a C_3 - C_{24} , saturated hydrocarbon chain, straight chain or branched; or an unsaturated C_3 - C_{24} , hydrocarbon chain, straight chain or branched, having 1 to 6 carbon-to-carbon double bonds;



wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^{13} , R^{15} and R^{19} , same or different, are C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched; or unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

40. The method in accordance with claim 39, wherein the substrate is a plurality of cords.

41. The method in accordance with claim 39, wherein the substrate is a polymeric sheet or fabric.

42. The method in accordance with claim 39, wherein the substrate is metal flat stock material.

43. A cord-reinforced article of manufacture comprising a plurality of cords selected from polymeric cords, metal cords, glass cords, and a combination thereof, adhered to the rubber composition of claim 1.

44. The rubber composition in accordance with claim 1, wherein the R^2 , R^5 , R^7 , R^{12} , R^{14} are fatty acid residues derived from animal or vegetable fatty acids.

45. The rubber composition in accordance with claim 44, wherein the fatty acids are selected from the group consisting of butter; lard; tallow; grease; herring; menhaden; pilchard; sardine; babassu; castor; coconut; corn; cottonseed; jojoba; linseed; oiticia; olive; palm; palm kernel; peanut; rapeseed; safflower; soya; sunflower; tall; tung; and mixtures thereof.

46. The rubber composition in accordance with claim 45, wherein the fatty acid residues are selected from the group consisting of hexanoic; octanoic; decanoic; dodecanoic; 9-dodecenoic; tetradecanoic; 9-tetradecenoic; hexadecanoic; 9-hexadecenoic; octadecanoic; 9-octadecenoic; 9-octadecenoic, 12-hydroxy; 9, 12-octadecadienoic; 9, 12, 15-octadecatrienoic; 9, 11, 13-octadecatrienoic; 9, 11, 13-octadecatrienoic, 4-oxo; octadecatetrenoic; eicosanoic; 11-eicosenoic; eicosadienoic; eicosatrienoic; 5, 8, 11, 14-eicosatetraenoic; eicosapentaenoic; docosanoic; 13-docosenoic; docosatetraenoic; 4, 8, 12, 15, 19-docosapentaenoic; docosahexaenoic; tetracosenoic; and 4, 8, 12, 15, 18, 21-tetracosahexaenoic.

47. The rubber composition in accordance with claim 1, wherein the ester is a combination of compounds having formula II, III and IV.

48. The rubber composition in accordance with claim 1, wherein the ester has formula III.

49. The rubber composition in accordance with claim 1, wherein the ester has formula IV.

STATEMENT UNDER PCT ARTICLE 19(1).

International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: 011-41-22-740-14-35

Attention: Authorized Officer Jan Boon

Ladies and Gentlemen:

Transmitted herewith are substitute sheets 67, 69, 72-79, and 79/1, which have been amended pursuant to Article 19 of the Patent Cooperation Treaty.

According to the amendments, claims 2, 3, 6-22, 24-38, 40-42, 45, and 46 have been amended and claims 47-49 have been added. Claims 1, 4, 5, 23, 39, 43, and 44 remain unchanged by these amendments. The claims have not been renumbered.

Support for the amendments may be found variously throughout the application. More specifically, claims 2, 3, 6-22, 24-38, 40-42, 45, and 46 have been amended merely to correct typographical errors.

Support for the added claims 47-49 may be found variously throughout the application. More specifically, support for added claim 47-49 may be found, for example, in original claim 1 of the present application. No new matter has been added.

Entry of the foregoing amendments is earnestly solicited.

Respectfully submitted,

MARSHALL, GERSTEIN & BORUN LLP

November 17, 2003

By: Richard H. Anderson
Richard H. Anderson
Agent for Applicant
6300 Sears Tower
233 S. Wacker Drive
Chicago, Illinois 60606-6357
(312) 474-6300

11.17.03